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A COMPENDIOUS MANUAL
OF
QUALITATIVE CHEMICAL ANALYSIS.

BY

CHARLES W. ELIOT DEPARTMENT OF

**EDUCATION
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REVISED, WITH THE CO-OPERATION OF THE AUTHORS,

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PREFACE.

THE authors have endeavored to include in this short treatise enough of the theory and practice of qualitative analysis "in the wet way," to bring out all the reasoning involved in the subject, and to give the student a firm hold upon the general principles and methods of the art. It has been their aim to give only so much of mechanical detail as is essential to an exact comprehension of the methods and to success in the actual experiments. Hence, the multiplication of different tests or processes, having essentially the same object, has been purposely avoided. For the same reason none of the rare elements are alluded to. The manual is intended to meet the wants of the general student, to whom the study is chiefly valuable as a means of mental discipline and as a compact example of the scientific method of arriving at truth. To professional students who wish to make themselves expert analysts, this little book offers a logical introduction to the subject, an outline which is trustworthy as far as it goes, but which needs to be filled in and enlarged by the subsequent use of some more elaborate treatise as a book of reference. Prof. Johnson, of Yale, has supplied this need with his excellent edition of Fresenius's comprehensive manual.

The authors believe that they have put into the following pages as much of inorganic qualitative analysis as is useful for training, and also as much as the engineer, physician, agriculturist, or liberally educated man needs to know. The book has been written for the use of classes in the Institute of Technology, who have already studied the authors' "Manual of Inorganic Chemistry." It is simply an implement devised to facilitate the giving of thorough

instruction to large classes in the laboratory. It is the authors' practice to examine their classes orally every four or five exercises, in order to secure close attention to the reasoning of the subject. With this exception, the subject is studied exclusively in the laboratory, tools in hand. Fifty laboratory exercises of two hours each have proved sufficient to give their classes a mastery of the subject as it is presented in this manual.

It is scarcely necessary to say that this little work is a compilation from well-known authorities, among which may be particularly mentioned the works of Galloway, Will, Fresenius, and Northcote & Church.

BOSTON, April, 1869.

PREFACE TO THE REVISED EDITION.

IN this revised edition, undertaken with the advice and consent of the authors, such alterations and additions have been made as have been suggested by the use of the book with a number of classes in the laboratory.

W. R. N.

BOSTON, July, 1876.

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QUALITATIVE ANALYSIS.

INTRODUCTION.

1. **Qualitative Analysis**, in the widest sense of the term, is the art of finding out the elements contained in compound substances. The general definition has important limitations in practice. In the first place, the art, as commonly taught, applies almost exclusively to mineral, or inorganic, substances, and touches only incidentally upon the multifarious compounds of carbon with hydrogen, oxygen, nitrogen and a few other elements, which form the subject-matter of that branch of chemical science called organic chemistry. Again, the analysis of gases constitutes a distinct branch of analysis, requiring methods and apparatus of its own, and therefore to be most advantageously studied by itself. These deductions made, there remains the analysis of inorganic solids and liquids, which is in fact the main subject of qualitative analysis in the present technical sense of the term.

Of the sixty-three recognized chemical elements, only the thirty-four most important are embraced in the systematic course of this manual. Means of detecting a few other less common elements are incidentally given; but most of the elements which are so rare as to be at present of little interest except to the professional chemist or mineralogist are not alluded to.

2. Some previous knowledge of general chemistry is essential to the successful study of qualitative analysis. It is assumed that the student knows something of the common

elements and of their most important combinations, that he is familiar with the principal laws which govern chemical changes, and that he possesses a certain skill in the simplest manipulations. The tools and operations employed in qualitative analysis are few and simple; but neatness, method in working and a vigilant attention even to the minutest details, are absolutely essential. As the various substances used or produced in the operations of analysis will not be particularly described, the careful student will keep at hand some text-book on general chemistry, to which he can constantly refer to refresh his recollection of the formulæ and physical and chemical properties of the substances referred to. It should be observed that it is often very difficult—in fact, impossible in the present state of knowledge—to express in exact equations the involved or obscure reactions which occur in complex mixtures during the operations of analysis. It is a useful exercise for students to write out in equations the simpler chemical changes which occur in analysis; but when the attempt is made to put a complex reaction into numerical symbols, the equations are apt to express either more than we know, or less.

3. Although the detection of the elements contained in compound substances is the ultimate object of analysis, it is only by exception that the elements themselves are isolated, and recognized in their uncombined condition. An element is generally recognized through some familiar compound, whose apparition proves the presence of all the elements it contains, just as the presence of any word upon this page makes it sure that the letters with which it is spelt are imprinted there. If, as the result of a definite series of operations upon some unknown body, the hydrated oxide of iron be produced, no iron having been added during any stage of the process, the proof of the presence of iron in the original body is quite as certain as if the gray metal itself had been extracted from it. If some well-known sulphate, like sulphate of lead, or of barium, for example, result from a series

of experiments upon some unknown mineral, it is certain that the mineral contained sulphur ; provided only that no sulphur has been introduced in any of the chemical agents to whose action the mineral has been submitted.

The compounds through which the elements are recognized are necessarily bodies of known appearance, deportment and properties. They are, in fact, bodies of various, though always definite, composition ; oxides, sulphides, chlorides, sulphates and many other salts, are thus made the means of identifying one or more of the elements which they contain. The object of the analyst is to bring out from the unknown substance, by expeditious processes and under conditions which admit of no doubt as to their testimony, these identifying compounds, with whose appearance and qualities he has previously made himself acquainted. As he follows the course of experiments laid down in this manual, the student will gradually acquire, with the aid of frequent references to a text-book of general chemistry, that stock of information concerning the identifying compounds which must be always ready for use in his mind, and at the same time he will be made familiar with the character of the methodical processes which secure a prompt and sure testimony to the elementary composition of the substances he examines.

4. The subject is treated in two parts or divisions, of which the first contains a series of experiments to illustrate a systematic course of examination for substances in solution, when once that solution has been made ; while the second treats chiefly of the preliminary examination of solids and the means of bringing them into solution, and indicates the general methods to be pursued in the actual analysis of a substance of unknown composition.

PART FIRST.

CHAPTER I.

DIVISION OF THE METALLIC ELEMENTS INTO CLASSES.

5. **Example of the Separation of two Elements.** — Put a small crystal of nitrate of silver and a small crystal of sulphate of copper into a test-tube (Appendix, § 65), and dissolve them in two teaspoonfuls of water, warming the water at the lamp to facilitate the solution. Add to this solution a few drops of dilute chlorhydric acid (App., § 3). Shake the contents of the tube violently, wait until the curdy precipitate, which the acid produces, has separated from the liquid, and then add one more drop of chlorhydric acid. If this drop produces an additional precipitate, repeat the operation until the new drop of acid produces no change in the partially clarified liquid. Then, and not till then, has *all* the silver which the original solution contained been precipitated in the form of chloride of silver, an unemployd balance or *excess* of the *reagent*, chlorhydric acid, remaining in the clear liquid; this liquid can be readily separated by filtration from the curdy chloride.

Shake the contents of the test-tube, and transfer them as completely as possible to a filter (App., § 70), supported in a very small glass funnel (App., § 69), which has been placed in the mouth of a test-tube. With a wash-bottle (App., § 81) rinse into the filter that portion of the precipitate which has adhered to the sides of the first test-tube. When the

filtrate has drained completely from the precipitate, set the test-tube which has received it aside. Wash the precipitate together into the apex of the filter by means of a wash-bottle with a fine outlet; and, in order to wash out the soluble sulphate of copper which adheres to the precipitate, fill the filter full of water two or three times, throwing away this wash-water when it has passed through the filter.

The complete separation of the silver and copper which were mixed in the original solution is already accomplished; the silver is on the filter in the form of chloride; the copper is in the clear, bluish filtrate. This speedy and effectual separation of the two elements is based upon the fact that chloride of silver is insoluble in water and acid liquids, and is, therefore, formed when chlorhydric acid is added to a solution containing a salt of silver; chloride of copper, however, is readily soluble in water and acid liquids, and, even if formed by the addition of chlorhydric acid to a solution of a compound of copper, would fail to manifest itself by appearing as a precipitate. It is, in general, true that whenever, by the addition of a reagent, there can be formed in any solution a compound insoluble in the liquids present, this compound always separates as a precipitate. Such differences of solubility as are illustrated by the case of the chlorides of silver and copper are the chief-reliance of the analyst.

6. Definition of the term "Class." Class I. — In the foregoing experiment only two elements have been separated. It might obviously be very difficult, if not impossible, to find a special reagent for every element, which would always precipitate that single element and never any other. Chlorhydric acid, for example, which precipitates silver so admirably from any solution containing that element, is capable of eliminating two other elements under like conditions. The lower chloride of mercury (mercurous chloride or calomel) is insoluble in water and weak acids. Chloride of lead is sparingly soluble in cold water, and is still less soluble in water acidulated with chlorhydric acid. The chlorides of the

other metallic elements are all soluble in water and acids under the conditions of the analytical process.

There are embraced in the scope of this manual twenty-two of the so-called *metallic* elements,—elements whose hydrates or oxides are said to be *basic* in their character, and are collectively designated as bases: if chlorhydric acid were added in proper quantity to a solution imagined to contain all these elements, three, and only three, of the twenty-two elements would be precipitated as chlorides. After filtration and washing, a mixture of chloride of silver, chloride of lead and mercurous chloride would remain upon the filter, and all the other elements would have passed as soluble compounds into the filtrate. Silver, lead and mercury, the three elements thus separated from the rest by this well-marked reaction with chlorhydric acid, constitute a *class*, the first of several classes into which the metallic elements are divided for the ends of qualitative analysis. Each class is characterized by some clear reaction which suffices, when intelligently applied, to separate the members of any one class from the other classes. The chemical agent, by means of which this distinctive reaction is exhibited, is called the *general reagent* of the class. Thus, chlorhydric acid is the general reagent of the first class.

This division of the elements into classes renders it unnecessary to find means of separating each individual element from *all* the others. In the systematic course of an analysis, the classes are first sought for and separated; afterwards each class is treated by itself for the detection of its individual members. It is an incidental advantage of this division of the elements into classes that, when the absence of any whole class has been proved by the failure of its peculiar general reagent to produce a precipitate in a solution under examination, it is unnecessary to search further for any member of that class. Much time is thus saved, for it is as easy to prove the absence of a class as of a single element. The full treatment of the first class of elements, comprising, as

we have seen, silver, lead and mercury, is the subject of Chapter II.

7. Experiment to Illustrate the Division of the Metallic Elements into Classes. — We proceed to demonstrate experimentally the chemical facts upon which rests the division of the other metallic elements into convenient classes.

Prepare a complex solution, by mixing together in a small beaker (App., § 68) a small teaspoonful of each of the following solutions (App., § 62), viz. : — chloride of copper, arsenious acid in chlorhydric acid, ferrous chloride, chloride of zinc, chloride of calcium, chloride of magnesium and chloride of sodium. Dilute the mixture thus prepared with its own bulk of water. Should any turbidity or precipitate appear, add chlorhydric acid, little by little, until the solution becomes clear. This solution is representative; it contains at least one member of each of the classes of elements which remain to be defined. It contains no member of the first class; but we may consistently suppose that the members of this class have been previously precipitated, as in the foregoing experiment (§ 5), and that an excess of chlorhydric acid remains in the liquid.

8. Definition of Classes II and III. — Pass a slow current of sulphuretted hydrogen (App., § 14) from a gas-bottle or self-regulating generator through the acid liquid in the beaker. This operation must be performed either out of doors or in a current of air sufficient to carry the excess of the gas away from the operator. A dense, dark colored precipitate will immediately appear, and gradually increase in bulk. When the gas has flowed continually for five or ten minutes through the liquid, remove the beaker from the source of the gas (or interrupt the stream of gas if a self-regulating generator be employed), stir the liquid well, and blow out the sulphuretted hydrogen which lies in the beaker. If after the lapse of two or three minutes the liquid smells distinctly of sulphuretted hydrogen, it is saturated with the gas, and it is sure that the reagent has done its work. If the liquid does not retain the

characteristic odor, the gas must be again passed through it until saturation is certainly attained.

In order to obtain still further assurance of the saturation of the liquid, it is often well to take the first portions of the filtrate of the succeeding paragraph and add a small quantity of sulphuretted hydrogen water (App., § 15). If a sufficient amount of the gas had not been passed into the liquid, the addition of the sulphuretted hydrogen water would cause the appearance of a precipitate. In such a case the filtered portion must be returned to the beaker and the stream of gas again passed through the liquid.

Pour the contents of the beaker, well stirred up, upon a filter which is supported over a test-tube or second beaker. Rinse the first beaker once with a teaspoonful of water, and transfer this rinsing water to the filter, allowing the filtered liquid to mix with the original filtrate. Label* this filtrate "Filtrate from II and III" (classes), and preserve it for later study.

If any considerable quantity of precipitate has adhered to the sides of the original beaker, it may be detached and washed on to the filter by means of a sharp jet of water from the wash-bottle. The precipitate, as it lies upon the filter, must then be washed once or twice with water; the wash-water

* The student should at once make it a rule to label every filtrate or precipitate which he has occasion to set aside, even for a few moments. A bit of paper large enough to carry a descriptive symbol or abbreviation should be attached to the vessel which contains the liquid or precipitate. Paper gummed on the back or the small labels which are sold already gummed are convenient for this use.

This habit, once acquired, will enable the student to carry on simultaneously without error or confusion, several operations. He may be throwing down one precipitate, washing another, filtering a third, and dissolving a fourth at the same time, and the four processes may belong to as many different stages of the analysis. There will be no danger of error if labels are faithfully used; and a great deal of time will be saved. The unaided memory is incapable of doing such work with that full certainty, admitting of no suspicion or after-qualms of doubt, which is alone satisfying, or indeed admissible, in scientific research.

is thrown away. The washed precipitate consists of a mixture of sulphide of copper (CuS) and tersulphide of arsenic (As_2S_3). The fact that these sulphides are precipitated under the conditions of this experiment proves that they are both insoluble in weak acid liquors. They are also both insoluble in water. But an important difference between the two sulphides nevertheless exists, a difference which affords a trustworthy means of separating one from the other.

When the water has drained away from the precipitate, open the filter upon a plate of glass, and gently scrape the precipitate off the paper with a spatula of wood or horn. Place the precipitate in a small porcelain dish (App., § 73), pour over it enough of a solution of sulphhydrate of sodium (App., § 23) to somewhat more than cover it, and heat the mixture cautiously to boiling, stirring it all the time with a glass rod. The quantity of sulphhydrate of sodium to be employed varies, of course, with the bulk of the precipitate; in this case two or three teaspoonfuls will probably suffice. It is very undesirable to use an unnecessarily large quantity of the reagent for reasons that will hereafter appear. A portion of the original precipitate remains undissolved; but a portion has passed into solution. Filter the hot liquid again. The black residue on the filter is sulphide of copper, which is insoluble, not only in water and weak acids, but also in alkaline liquids. To the filtrate, collected in a test-tube, add gradually chlorhydric acid, until the liquid has an acid reaction on litmus paper (App., § 58). A yellow precipitate of sulphide of arsenic will appear as soon as the alkaline solvent which kept it in solution is destroyed. The sulphide of arsenic differs from the sulphide of copper in that it is soluble in alkaline liquids.

In this series of experiments copper and arsenic stand, not as isolated elements, but as representatives of classes. The following common elements have sulphides which are insoluble in water, weak acids *and* alkaline liquids:—Lead, mercury, bismuth, cadmium and copper. These elements constitute Class II in our system of analysis. The following elements

have sulphides which are insoluble in water and weak acids, but soluble in alkaline liquids:—Arsenic, antimony, tin (and the precious metals gold and platinum). These elements constitute Class III. If all the elements of both groups had been present in the original solution, one class might have been separated from the other by the same process employed in the case of the representative elements, arsenic and copper.

The question may naturally suggest itself, how it happens that lead and mercury are included in Class II, when they were both precipitated in Class I. The chloride of lead, which is thrown down by chlorhydric acid, is not wholly insoluble in water; hence it happens that the lead is not completely precipitated in Class I. That portion of the lead which has escaped precipitation as chloride in Class I, will be thrown down as sulphide in Class II, for the sulphide of lead is insoluble in water, weak acids and alkalis. In regard to mercury, it will be remembered that there are two sorts of mercury salts, mercurous salts and mercuric salts. The mercurous chloride, Hg_2Cl_2 , (*calomel*) is insoluble in water; but the mercuric chloride, HgCl_2 , (*corrosive sublimate*) is soluble in water. If, therefore, mercury be present in the form of some mercurous salt, it will be separated as mercurous chloride in Class I. If, on the contrary, it be present in the form of some mercuric salt, it will be separated in Class II as mercuric sulphide (HgS), for this sulphide is insoluble in water, weak acids and alkaline liquids. If a mixture of mercurous and mercuric salts be contained in the original solution, mercury will appear both in Class I and in Class II.

The treatment of Class II is fully discussed in Chapter III. The separation of Class III and the means of separating the members of the class, each from the others, form the subject of Chapter IV.

9. Definition of Class IV.—We now return to the study of the filtrate from Classes II and III. Pour the liquid into a small evaporating dish, and boil it gently for five or six minutes to expel the sulphuretted hydrogen with which the

fluid is still charged. To make sure that all the gas is expelled, hold a bit of white paper moistened with a solution of acetate of lead (App., § 46) over the boiling liquid; when the paper remains white, all the sulphuretted hydrogen is gone. Next, add to the liquid in the dish ten or twelve drops of strong nitric acid (App., § 4), and again gently boil the liquid for three or four minutes, in order that all the iron present may be converted into ferric salts. Then pour the liquid into a test-tube, add to it about one third its bulk of chloride of ammonium (App., § 19), and finally add ammonia-water (App., § 16), little by little, until the mixture, after being well shaken, smells decidedly of ammonia. A brownish-red precipitate of hydrated sesquioxide^{*} of iron will separate from the liquid. Pour the contents of the test-tube upon a filter, rinse the tube and the precipitate once with a little water, and preserve the whole filtrate for subsequent operations.

Two other metals, aluminum and chromium, are precipitated, as iron has here been, by ammonia-water under the same conditions and in the same form, viz., as hydrates. These three elements, therefore, constitute the fourth class, whose treatment forms the subject of Chapter V. The hydrates of these elements are insoluble in water, *even in the presence of salts of ammonium*, such as the chloride of ammonium which has been expressly added, and the nitrate of ammonium which has been formed during the neutralization of the acid liquid. The student may be curious to know why the presence of ammonium salts is insisted upon before the elements of this class are thrown down by ammonia-water. The ammonium salts have nothing to do with the precipitation of iron, aluminum and chromium; but by their presence they prevent the precipitation, as will be hereafter explained, of certain other elements whose hydrates, though but slightly soluble in water, are dissolved by solutions of ammonium salts. The salts of ammonium are therefore added to keep in solution certain other elements which otherwise would encumber Class IV.

* ($2Fe_2O_3, 3H_2O$)

10. Definition of Class V. — We now proceed to the examination of the filtrate from the precipitate of Class IV. Bring this liquid to boiling in a test-tube, and add sulphurate of ammonium (App., § 17), little by little, to the boiling liquid as long as a precipitate continues to be formed. To make sure that the precipitation is complete, shake the hot contents of the test-tube strongly, and then allow the mixture to settle until the upper portion of the liquid becomes clear. Into this clear portion let fall a drop of sulphurate of ammonium; when this drop produces no additional precipitate, the precipitation is complete. Filter off the whitish precipitate of sulphide of zinc, and preserve the filtrate for further treatment. It sometimes happens that this precipitate refuses to settle and leave the upper portion of the liquid sufficiently clear to test in the manner described above; in this case a small portion of the mixture may be filtered and a drop of sulphurate of ammonium added to the clear filtrate in order to determine whether the precipitation is complete. If not, the filtered liquid must be returned to the flask and more of the reagent added.

The element zinc, representing a new class of elements, is precipitated under the conditions of the above experiment, because its sulphide, though soluble in dilute acids, is insoluble in alkaline liquids. The metals manganese, nickel and cobalt resemble zinc in this respect, and these four elements therefore form a new class, Class V, in this analytical method. The representative sulphide of this class was not precipitated by the sulphuretted hydrogen when that reagent was employed to throw down the members of the Classes II and III, because the solution was at that time acid. Again it was not precipitated with Class IV by the ammonia-water, because the sulphuretted hydrogen with which the solution had previously been charged, was expelled by boiling before the ammonia-water was added. The complete treatment of Class V forms the subject of Chapter VI.

11. Definition of Class VI. — Add to the filtrate from Class V, two or three teaspoonfuls of carbonate of ammonium (App., § 18) and boil the solution. A white precipitate of carbonate of calcium will be produced. After boiling, allow the precipitate to settle until the upper portion of the liquid is comparatively clear. To this clarified portion add a fresh drop of carbonate of ammonium. If this drop produce an additional precipitate, more carbonate of ammonium must be added, and the boiling repeated. To the partially clarified liquid add again a drop of carbonate of ammonium. This process of making sure of the complete precipitation of the calcium is essentially the same as that prescribed in precipitating the last class, and is, indeed, of general application. When the precipitation of the calcium has been proved to be complete, filter the whole liquid, and receive the filtrate in a small evaporating-dish. Calcium is separated in the form of carbonate under these circumstances, because this carbonate is almost insoluble in weak alkaline liquids, when an excess of carbonate of ammonium is present. The allied elements barium and strontium behave in the same way, so that these three elements, viz., barium, strontium and calcium, compose a new class — Class VI, whose complete treatment is set forth in Chapter VII.

12. Definition of Class VII. — Of the twenty-two metallic elements, which were to be classified (§ 6), only three remain, viz., magnesium, sodium and potassium. It is obvious that these three elements could not have remained in solution through all the operations to which the original liquid has been submitted, unless their chlorides and sulphides had been soluble in weak acids, and their oxides (or hydrates), sulphides and carbonates soluble in dilute ammonia-water, at least in presence of dilute solutions of ammonium salts. It is a fact that all these compounds of sodium and potassium are soluble in water, and in weak acid, alkaline, and saline solutions; the magnesium would have been partially precipitated in Classes IV, V and VI, but for

the presence of ammonium salts in the solution. These three elements constitute Class VII.

Evaporate the filtrate from Class VI until it is reduced to one half or one third of its original bulk. Pour a small part of the evaporated filtrate into a test-tube; add a little ammonia-water and a teaspoonful of phosphate of sodium (App., § 26), and shake the contents of the tube violently. Sooner or later a crystalline precipitate will appear. This peculiar white precipitate of phosphate of magnesium and ammonium identifies magnesium; but as we have added a reagent containing sodium, the filtrate is useless for further examination. The liquid remaining in the evaporating-dish is then evaporated to dryness, and moderately ignited until fuming ceases. All the ammoniacal salts which the solution contained will be driven off by this means, and there will remain a fixed residue, in which are concentrated all the salts of magnesium and sodium which the solution contained. In this case we have already proved the presence of magnesium; it remains to indicate briefly the nature of the means used to detect the sodium.

Dissolve the residue in the dish, or a portion of it, in three or four drops of water. Dip a clean platinum wire (App., § 79) into this solution, and introduce this wire into the colorless flame of a gas or spirit-lamp (App., § 74). An intense yellow coloration of the flame demonstrates the presence of sodium. A violet coloration would have proved the presence of potassium. Magnesium compounds, when present, have no prejudicial effect on these characteristic colorations. The means of detecting each member of this last class in presence of the others will be found described in Chapter VIII.

13. A condensed statement of the classification illustrated by the foregoing experiments is contained in the table on the next page. All the common metallic elements are embraced in it. The place of the precious metals gold and platinum is also indicated. The classification itself would

THE SEVEN CLASSES OF THE METALLIC ELEMENTS.

CLASS I.	CLASS II.	CLASS III.	CLASS IV.	CLASS V.	CLASS VI.	CLASS VII.
Precipitated as chlorides. As Pb Hg	Precipitated as sulphides insoluble in dilute acids, and not redissolved by alkalis. Pb Hg Bi Cd Cu	Precipitated as sulphides insoluble in dilute acids, but redissolved by alkalis. As Sb Sn [Au] [Pt]	Precipitated by ammonia-water, usually as hydrates. Fe Al Cr [together with certain salts which require an acid solvent.]	Precipitated as sulphides insoluble in alkaline fluids. Zn Mn Ni Co	Precipitated as carbonates. Ca Ba Sr	Remaining elements. Distinguished by special tests. Mg Na K

not be essentially different, if all the rare elements were comprehended in it. The general subdivisions would be the same, although some of them would embrace many more particulars.

14. It is essential to success to follow precisely the prescribed *order* in applying the various general reagents. Class I would go down with Class II, were chlorhydric acid forgotten as the first general reagent. Class II would be precipitated in part with Class IV and in part with Class V if sulphuretted hydrogen were not used in its proper place. A large number of the members of the first five classes would be precipitated as carbonates with Class VI, were they not previously eliminated by the systematic application of chlorhydric acid, sulphuretted hydrogen, ammonia-water and sulphhydrate of ammonium in the precise order and under the exact conditions above described. It should be noticed that all the general reagents are volatile substances, which can be completely removed by an evaporation to dryness followed by a very moderate ignition.

15. The series of experiments just completed is merely intended to demonstrate the principles in accordance with which these twenty-two common elements are classified for the purposes of qualitative analysis. The general plan is here sketched; the practical details, essential to success in the conduct of an actual analysis, will be given hereafter.

CHAPTER II.

CLASS I.—ELEMENTS WHOSE CHLORIDES ARE INSOLUBLE IN WATER AND ACIDS.

16. Example of the Precipitation of the Members of Class I.— Place in a test-tube five or six drops of a tolerably concentrated aqueous solution of nitrate of silver (App., § 62), an equal quantity of a solution of mercurous nitrate and two teaspoonfuls of a solution of nitrate of lead. In case the solution becomes turbid through the action of carbonic acid dissolved in the water, pour in one or two drops of nitric acid to destroy the cloudiness.

Add dilute chlorhydric acid to the solution, drop by drop, and shake the mixture thoroughly after each addition of the acid, until the fresh portions of the latter cease to form any precipitate on coming in contact with the comparatively clear liquor which floats above the insoluble chlorides. Finally, add three or four more drops of the acid to insure the presence of an excess of it in the solution.

17. Analysis of the Mixed Chlorides.— The following method of separating the chlorides of lead, silver and mercury, one from another, depends upon the facts:— 1st. That chloride of lead, though but little soluble in cold water, dissolves readily in boiling water, while chloride of silver and subchloride of mercury (*mercurous chloride*, Hg_2Cl_2), are as good as insoluble in that liquid; 2d. That chloride of silver is soluble in ammonia-water; and 3d. That mercurous chloride is discolored by ammonia-water without dissolving.

To effect the separation:— Collect upon a filter the precipitate produced by chlorhydric acid, allow it to drain, and rinse it with a few drops of cold water. Place a clean test-tube beneath the funnel which contains the filter and precip-

itate, thrust a glass rod through the apex of the filter, and wash the precipitate off the filter into the test-tube by means of a wash-bottle which throws a fine stream.

Heat the mixture of water and precipitate to boiling, then allow the precipitate to settle and pour off the hot liquor upon a new filter, taking care to retain the precipitate as far as possible in the tube. To the clear filtrate add two or three teaspoonfuls of dilute sulphuric acid. (App., § 9.) A white cloud of sulphate of lead will be formed in the midst of

Test the liquid. In case the precipitate contains a large
for proportion of chloride of lead, it may happen that
Pb. the hot water will take up so much of it that crystals of the chloride will separate from the clear aqueous solution as it becomes cold, or that the liquor will be rendered cloudy by the deposition of numerous small particles of the chloride.

Pour a fresh quantity of water upon the precipitate which was retained in the test-tube, boil the mixture and, after allowing the precipitate to subside, pour the nearly clear liquid upon the same filter as before. This operation of boiling the precipitate with successive portions of water is performed in order to insure the complete removal of the chloride of lead; the liquid is filtered through the same filter in order to retain any particles of the precipitate which fail to settle in the tube, but it is not necessary to save this wash-water as most of the chloride of lead was obtained in the filtrate from the first boiling.

After the mixed precipitate of chloride of silver and mercurous chloride has been thus boiled with water several times, cover it with several teaspoonfuls of ammonia-water, heat the mixture to boiling, and pour it upon the filter used in the last paragraph: the filtrate is to be received in a clean test-tube. The chloride of silver, dissolved by the ammonia-water, will pass into the filtrate, while the mercurous chloride suffers decomposition, and is converted into an obscure compound of mercury, chlorine, nitrogen and hydrogen, which remains upon the filter in the form of an insoluble black or gray powder.

To confirm the presence of silver, add to the filtrate dilute nitric acid (App., § 5), until the solution will redden litmus paper: the chloride of silver is reprecipitated unchanged as soon as the alkaline solvent is neutralized.

Test
for
Ag.

To confirm the presence of mercury, the metal itself may be set free by heating the dry residue with carbonate of sodium (App., § 24) in a glass tube. To ensure the success of this experiment, wash into the lowest point of the filter the whole of the black residue. As soon as the last drops of liquid have drained from the filter, dry the latter, either in a dish upon a water-bath, or by spreading it open upon a ring of the iron stand (App., § 76) placed high above a small flame of the gas-lamp. When the precipitate is completely dry, scrape it from the paper, mix it with an equal bulk of carbonate of sodium previously dried over the gas-lamp on platinum foil (App., § 79) and transfer the mixture to the bottom of a glass tube, No. 4 (App., § 82), closed at one end. Then wipe out the inside of the tube with a tuft of cotton fixed to a wire, or with a twisted slip of paper, and heat the closed end of the tube for two or three minutes in the flame of a gas-lamp. A sublimate of finely divided metallic mercury will form upon the walls of the tube; it will cohere to visible globules when scratched with a piece of iron wire.

Test
for
Hg.

18. An outline of the operations described in the foregoing paragraphs may be presented in tabular form, as follows:—

The General Reagent (HCl) of Class I precipitates $PbCl_2$, $AgCl$ and Hg_2Cl_2 . When the precipitate is boiled with water:—		
$PbCl_2$ goes into solution. Confirm presence of lead by precipitation of sulphate of lead.	$AgCl$ and Hg_2Cl_2 remain undissolved. On treating the mixture with ammonia-water:—	
	<table border="1" style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> $AgCl$ dissolves. Confirm presence of silver with nitric acid. </td> <td style="width: 50%; vertical-align: top;"> A black compound of Hg remains undissolved. Confirm presence of Hg by isolating the metal. </td> </tr> </table>	$AgCl$ dissolves. Confirm presence of silver with nitric acid.
$AgCl$ dissolves. Confirm presence of silver with nitric acid.	A black compound of Hg remains undissolved. Confirm presence of Hg by isolating the metal.	

19. In the actual analysis of a solution of unknown composition, a precipitate might under certain circumstances be formed on the addition of chlorhydric acid, even in the absence of all members of Class I. This might occur in case the liquid under examination contained a hyposulphite; for this class of salts is decomposed, with evolution of sulphurous acid and deposition of sulphur, on the addition of the general reagent HCl of Class I. Some sulphides also are decomposed by chlorhydric acid, with deposition of sulphur. A gelatinous white precipitate of hydrated silicic acid might also be formed at this stage in certain circumstances, as will be explained hereafter (§§ 69 & 86, I. c, a).

CHAPTER III.

CLASS II.—ELEMENTS WHOSE SULPHIDES ARE INSOLUBLE IN WATER, DILUTE ACIDS AND ALKALIES.

20. Example of the Precipitation of the Members of Class II.—Place in a small beaker a half teaspoonful of a solution of each of the following substances:—mercuric chloride (*corrosive sublimate*), chloride of bismuth, of cadmium, and of copper, together with two or three teaspoonfuls of a cold aqueous solution of chloride of lead. Fill the beaker half full of water, and add, drop by drop, enough strong chlorhydric acid to redissolve the basic chloride of bismuth which the water precipitates.

Heat the liquid in the beaker nearly or quite to boiling, then place the beaker beneath a chimney or in a strong draught of air, and saturate the solution with sulphuretted hydrogen gas. To determine when enough sulphuretted hydrogen has been passed through the liquid, remove the beaker every four or five minutes from the source of the gas, blow away the gas which lies in the beaker above the liquid, and stir the latter thoroughly with a glass rod. If, after the lapse of two or three minutes, the liquid still smells strongly of sulphuretted hydrogen, it is saturated with the gas and ready to be filtered. But in case no persistent odor of sulphuretted hydrogen is observed, the gas must be passed anew through the liquor until it has become fully saturated. Since some of the substances above enumerated are thrown down more quickly by sulphuretted hydrogen than the others, it is absolutely necessary to employ the reagent *in excess* in order that those members of the class which are least easily precipitated may not escape detection.

21. Analysis of the Mixed Sulphides.—The following method of separating the members of Class II depends upon

the facts:— 1st. That mercuric sulphide is insoluble in hot dilute nitric acid, while the other sulphides are converted thereby into soluble nitrates. 2d. That sulphate of lead is insoluble in acidulated water, while the sulphates of the other members of the class are soluble. 3d. That hydrate of bismuth is insoluble in ammonia-water, while the hydrates of cadmium and copper are soluble in that liquid. 4th. That hot dilute sulphuric acid converts the sulphide of cadmium into the soluble sulphate of cadmium while sulphide of copper is not affected by this reagent.

To effect the separation:— Collect the precipitated sulphides upon a filter; wash the precipitate *thoroughly* with successive portions of water until the wash-water is no longer acid to litmus paper; transfer the precipitate to a small porcelain dish, pour upon it four or five times as much dilute nitric acid as would be sufficient to cover it, and boil the mixture during two or three minutes, stirring it constantly with a glass rod, and adding water or dilute nitric acid at intervals to replace the liquid which evaporates. All the sulphides with the exception of the sulphide of mercury are decomposed and the several elements go into solution as nitrates; the sulphide of mercury, mixed with some free sulphur resulting from the decomposition of the other sulphides, remains undissolved, as a heavy dark-colored mass. Decant the nitric acid solution into a filter, collect the filtrate in a second porcelain dish, and evaporate it nearly to dryness in order to drive off the greater part of the free nitric acid before examining it for the elements supposed to be contained in it.

The residue insoluble in nitric acid which was left in the first dish, is to be washed with water in order to remove the adhering solution. This may generally be done by pouring water into the dish, allowing the precipitate to settle and then decanting the wash-water; it is sometimes necessary, however, to collect the precipitate on a filter and wash in the ordinary manner. In either case the wash-water is thrown away and the precipitate is boiled in the porcelain dish with as much aqua regia (App, § 6) as will barely cover

Dilute the acid solution obtained with an equal volume of water, remove from it, by filtration or otherwise, any particles of free sulphur which may remain undissolved, and add to it almost, but not quite, enough ammonia-water to neutralize its acidity. In case of the accidental addition of too much ammonia-water, manifested by the appearance of a precipitate and by the alkaline reaction on litmus, the solution must be made just acid by the cautious addition of nitric acid, a drop at a time. Place in the slightly acid solution a small bit of bright copper wire, and observe that metallic mercury is deposited upon the copper as a white silvery coating. After the lapse of ten or fifteen minutes, dry the wire upon blotting paper, drop it into a narrow glass tube which has been sealed at one end, and heat it at the lamp. Test
for
Hg. Metallic mercury will sublime, and be deposited as a dull mirror upon the cold portions of the glass. By scratching the sublimate with the point of a bit of iron wire, the metal may be made to collect into visible globules.

When the greater part of the free nitric acid has, by the aforesaid evaporation, been driven off from the filtrate which contains the mixed nitrates of lead, bismuth, cadmium and copper, transfer the residual liquor to a test-tube, mix it with two or three times its volume of dilute sulphuric acid, and leave the mixture at rest during fifteen or twenty minutes. Test
for
Pb. Sulphate of lead will be thrown down as a white powder, plainly to be seen in the test-tube, though it would have been scarcely visible in the white dish.

Collect the filtrate from the sulphate of lead in a small beaker, and add to it ammonia-water by repeated small portions, taking care to stir the liquid thoroughly after each addition of the ammonia, until a strong, persistent odor of the latter is perceptible. The hydrates of copper, cadmium, and bismuth will all be thrown down at first, but the hydrates of copper and cadmium will redissolve in the excess of ammonia-water, and hydrate of bismuth will alone be left as an insoluble precipitate. The blue color of the solution is due to the presence of copper. If in the case of the actual examination

of a solution of unknown composition no precipitate falls on the addition of ammonia-water, this does not prove the absence of copper and cadmium, as the hydrates may be dissolved by the ammonia-water as fast as formed, and thus escape observation.

To prove that the precipitate contains bismuth:—Collect it upon a filter, allow it to drain, and dissolve it in the smallest possible quantity of strong chlorhydric acid poured drop by drop upon the sides of the filter; carefully evaporate the acid solution to the bulk of two or three drops, and pour it into a large test-tube nearly full of water.

Test for Bi. A dense, milky cloud of insoluble basic chloride of bismuth will appear in the water. Since sulphate of lead is not absolutely insoluble in water which contains nitric acid, a slight precipitate of hydrate of lead might be produced on the addition of the ammonia-water even when no bismuth was present in the solution. To prove the presence of bismuth, the oxychloride must always be carefully tested for. It is to be remarked that if the amount of hydrate of bismuth is in any case small, considerable care must be exercised in applying the confirmatory test. In such a case the basic chloride may appear as white threads marking the path of the heavier liquid through the water, and gradually producing more or less turbidity throughout the whole mass of the water.

The blue color of the ammoniacal filtrate from the hydrate of bismuth indicates the presence of copper, and when well defined is of itself a sufficient proof of the presence of this element. But in the absence of a marked blue coloration, at this stage, copper should be specially tested for in the manner described below.

To separate the cadmium from the copper, proceed as follows:—Transfer the ammoniacal filtrate to a glass flask, heat it to boiling, and drop into the boiling liquid sulphhydrate of ammonium as long as a precipitate continues to be formed. In order to be sure that the precipitation is complete, remove the flask from the lamp at intervals, shake it strongly, and allow its contents to settle, so that a comparatively clear

liquid may appear at the top, and into this clear liquid pour a drop of the sulphhydrate.

As a general rule, the operations of boiling and agitating tend to increase the coherency of precipitates, and to render them in some sense granular, so that they separate completely from the liquid in which they form, leaving it clear and susceptible of rapid filtration.

Collect the precipitate upon a filter, rinse it once or twice with water, and allow it to drain; then transfer the precipitate to a porcelain dish and cover it liberally with dilute sulphuric acid (App., § 10), made by mixing one part by measure of the strong acid with five parts of water. Heat the mixture until it actually boils; then pour the boiling liquor upon a filter, and collect the clear filtrate in a beaker. By hot dilute sulphuric acid of the prescribed strength, sulphide of cadmium is converted into sulphate of cadmium which dissolves in the acid liquid, while the black sulphide of copper remains intact. It is essential that the mixed precipitate of sulphide of copper and sulphide of cadmium do not remain upon the filter for any great length of time; for in such a case the sulphide of copper might become partially oxydized and dissolve in the dilute sulphuric acid, along with the sulphate of cadmium, thus obscuring the test for the latter element.

To prove the presence of cadmium, add ammonia-water to the acid filtrate until the liquid is alkaline; then add sulphhydrate of ammonium, and observe that the liquid immediately becomes cloudy from the presence of minute particles of sulphide of cadmium of characteristic yellow color. After some time this precipitate will collect at the bottom of the liquid.

To prove the presence of copper, in case no blue coloration was visible in the filtrate from hydrate of bismuth, transfer the black precipitate, insoluble in dilute sulphuric acid, to an evaporating-dish, dissolve it in a few drops of boiling, concentrated nitric acid, remove and wash the spongy mass of sulphur which is set free, neutralize the nitric acid with ammonia-

water, acidify the solution with acetic acid (App., § 12), transfer it to a test-tube, and add one or two drops of a solution of ferrocyanide of potassium (App., § 33). A peculiar reddish-brown precipitate of ferrocyanide of copper will fall in case much copper be present, and even when the proportion of copper in the solution is extremely small, a light brownish-red cloudiness will be produced.

In the absence of copper, yellow sulphide of cadmium would at once be thrown down by the sulphhydrate of ammonium, when this reagent is added to the filtrate from the hydrate of bismuth; and no further evidence of the presence of cadmium would be required.

22. The operations above described may be presented in tabular form as follows:—

<p>The General Reagent (H_2S) of Class II precipitates HgS, PbS, Bi_2S_3, CdS and CuS (as well as members of Class III, which are subsequently separated by solution in sulphhydrate of sodium). The precipitate is boiled with nitric acid:—</p>				
<p>A residue of HgS, mixed with S, remains. Confirm presence of Hg with copper wire.</p>	<p>Pb, Bi, Cd and Cu go into solution as nitrates. On adding dilute sulphuric acid to the concentrated solution:—</p>			
	<p>$PbSO_4$ is thrown down. [Confirm the presence of Pb by converting $PbSO_4$ into $PbCrO_4$.]</p>	<p>The sulphates of Bi, Cd and Cu remain in solution. On adding an excess of ammonia-water:—</p>		
		<p>Hydrate of Bismuth is thrown down. Confirm Bi by precipitating the oxychloride.</p>	<p>Compounds of Cd and of Cu remain in solution. Throw down CdS and CuS with $(NH_4) HS$. and boil with dilute sulphuric acid:—</p>	
			<p>$CdSO_4$ goes into solution. Confirm presence of Cd by precipitation of CdS.</p>	<p>CuS remains undissolved. Confirm presence of Cu by testing with ferrocyanide of potassium.</p>

23. The Method of Separating Class I from Class II has already been particularly described in § 6. It should be observed, however, that even if no member of Class I were present in the mixture to be analyzed, it would still be necessary to acidulate the liquid with chlorhydric acid, before passing the sulphuretted hydrogen, in order to prevent the precipitation of members of Classes IV and V, and to secure the complete precipitation of members of Class III.

The liquid should be watched attentively when the stream of sulphuretted hydrogen first begins to flow through it, since useful inferences may often be drawn from the various phenomena which present themselves.

a. Thus, the formation of a white precipitate which afterwards changes to yellow, orange, brownish-red, and finally to black, as the liquid gradually becomes saturated with the gas, indicates the presence of mercuric chloride. The white precipitate at first formed is a compound of chloride and sulphide of mercury ($\text{HgCl}_2\cdot 2\text{HgS}$), but by the action of successive portions of sulphuretted hydrogen, the composition and appearance of the precipitate is changed, until it has been completely converted into black sulphide of mercury. It is important that the mercury should be completely converted into sulphide as the compound just mentioned is soluble in nitric acid; the result is rendered more certain if the solution be warmed before being treated with sulphuretted hydrogen.

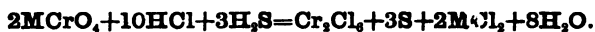
b. If the precipitate is of a dull red color at first, afterwards changing to black, the probable presence of lead is indicated; for sulphuretted hydrogen throws down from solutions which contain much free chlorhydric acid a red compound of chloride of lead and sulphide of lead, which is afterwards decomposed, with formation of the black sulphide, when the solution becomes saturated with the gas.

c. A decided bright yellow precipitate would indicate the presence of cadmium, arsenic or tin; of these three, cadmium is distinguished by the fact that its sulphide remains undis-

solved when the precipitate is treated with sulphhydrate of sodium to separate the members of Class III.

But even from solutions which contain no members of Classes II or III, yellow-white or milky-white precipitates of free sulphur are often thrown down; for sulphuretted hydrogen is easily decomposed, with deposition of sulphur, by a variety of oxidizing agents, such as nitric, chromic and chloric acids, and solutions of ferric salts and of free chlorine. If the solution under examination contained much nitric acid, sulphuretted hydrogen would have to be passed through it for a long time to destroy the acid, before the liquid could be saturated with the gas. In this case the sulphur separates as a tenacious mass of dirty yellow color; but in most instances, notably when the solution contains a ferric salt, the sulphur is precipitated in the form of exceedingly minute particles, which impart to the solution a peculiar milkiness or opalescence. These particles are so fine that they pass through the pores of filter paper; they cannot be removed by filtration.

If the original solution contains a chromate, its yellow or reddish-yellow color will be changed to green by the action of sulphuretted hydrogen; for the chromate is reduced to the condition of sesquichloride of chromium:—



The sulphur is set free in the form of the minute white particles above described, and remains suspended in the green liquid, looking not unlike a green precipitate.

d. The immediate formation of a black precipitate indicates the presence of copper or bismuth, and it is to be observed that either of these black precipitates would obscure the colors of the other sulphides of the class, and conceal them if present.

e. If no precipitate appears even when the liquid has become saturated with the gas, the absence of every member of Classes II and III is, of course, to be inferred.

CHAPTER IV.

CLASS III. — ELEMENTS WHOSE SULPHIDES ARE INSOLUBLE IN WATER OR DILUTE ACIDS, BUT SOLUBLE IN ALKALINE SOLUTIONS.

24. Example of the Precipitation of the Members of Class III. — Place in a small beaker six or eight drops of solutions of the chlorides of arsenic, antimony and tin. Pour in enough dilute chlorhydric acid to half fill the beaker, and, if need be, a sufficient number of drops of strong chlorhydric acid to dissolve any cloud of basic chloride of antimony which may appear in the liquor.

Pass sulphuretted hydrogen gas through the solution, in the manner described in § 20, until the odor of the gas persists. Then collect the precipitated sulphides upon a filter, and rinse the precipitate once or twice with water.

In the analysis of any complex solution of unknown composition which might contain one or all of the members of Class III, the sulphides of this class would, of course, all be thrown down at the same time as those of Class II. (Compare §§ 8, 22.) It will be well, therefore, for the sake of illustration, for the student to dissolve the present precipitate in sulphhydrate of sodium in order that he may begin the treatment of Class III at the precise point at which this class would be encountered in an actual analysis; namely, with the sulphides of the class in alkaline solution. To this end, allow the washed precipitate to drain, spread out the filter upon a plate of glass, scrape the precipitate from the paper with a small spatula of platinum, horn or wood, and transfer it to a porcelain dish. Pour upon the precipitate two or three times as much of a solution of sulphhydrate of sodium

NH₄HS

as would be sufficient to cover it, and boil the mixture very cautiously, so as to avoid spattering. The precipitate will soon dissolve, and no solid matter will be left suspended in the solution, excepting a few fibres of the filter paper. It is such a solution as this which in an actual analysis is examined for members of Class III.

25. Analysis of the Mixed Sulphides. — The method here given of separating arsenic, antimony and tin depends: — 1st. Upon the oxidation of the several sulphides by means of nitric acid and nitrate of sodium, and the conversion of arsenic into a compound soluble in water while antimony and tin are converted into insoluble compounds; 2d. Upon the fact that the tin in the compound thus formed is set free in the metallic state when this compound is treated with zinc and chlorhydric acid, while the antimony under similar circumstances is in part reduced to metallic antimony and in part converted into antimoniuiretted hydrogen; 3d. Upon the solubility of tin in strong chlorhydric acid.

To effect the separation; — Add strong nitric acid to the sulphurate of sodium solution until the reaction is distinctly acid; a precipitate forms which consists partly of the sulphides of arsenic, antimony and tin, and partly of sulphur from the decomposition of the alkaline sulphurate. Without heeding the precipitate which separates, evaporate the acid mixture to the bulk of half a teaspoonful; then add solid carbonate of sodium *very cautiously* until further addition causes no further effervescence. Then add half a teaspoonful of a mixture of equal parts of carbonate and nitrate of sodium. Evaporate to dryness with constant stirring, and heat the mass until it fuses. Pour out the liquid mass, as far as may be possible, upon a bit of cold porcelain, and when it has cooled somewhat, transfer it, together with whatever can be detached from the dish in which the fusion was made, to a clean mortar and reduce it to powder. Return this powder to the porcelain dish and when the dish with its contents is *perfectly cold* pour in several teaspoonfuls of cold water and

allow the mixture to stand, stirring it from time to time, until that portion of the fused mass which could not be detached from the dish has softened and is in part dissolved; finally, filter the solution. By the treatment with nitric acid and nitrate of sodium the arsenic of the sulphide of arsenic has been converted into arseniate of sodium, a compound which is soluble in water and which passes into the filtrate together with the excess of nitrate and carbonate of sodium and some sulphate of sodium formed during the process. The antimony has been converted into antimoniate of sodium and the tin into the binoxide; these two compounds, being scarcely at all soluble in water, remain on the filter. This insoluble residue is examined for antimony and tin in a manner presently to be described.

To the filtrate add nitric acid, drop by drop, until the liquid shows a faintly acid reaction. If a precipitate appear it is probably a hydrate of tin, and its appearance is due to the fact that the ignition with nitrate of sodium was conducted at so high a temperature that a portion of the nitrate of sodium was converted into caustic soda, and this acting on the oxide of tin formed a certain amount of soluble stannate of sodium.

The precipitate, if any appear, is to be filtered off and added to the insoluble residue which awaits examination. To one half of the clear filtrate add ammonia-water to alkaline reaction, then a few drops of a prepared solution of sulphate of magnesium and chloride of ammonium (App., § 47) and set the mixture aside for twelve hours. The formation of a white, crystalline precipitate of arseniate of ammonium and magnesium is evidence of the presence of arsenic.

To the remainder of the filtrate which contains the arsenic, and which should contain *the smallest possible* quantity of free acid, add a small quantity of a solution of nitrate of silver. On the addition of the nitrate of silver a precipitate generally falls even in the absence of arsenic, owing to the fact that

Test
for
As.

the nitrate of sodium used in the fusion generally contains some chloride of sodium, and in order that the arsenic present may be converted into *arseniate of silver*, a small quantity of nitrate of silver must be added, over and above that necessary to remove the chlorine present. Four or five drops of the solution of nitrate of silver (App. § 39) will usually suffice. The precipitated chloride of silver is to be removed by filtration.

To the clear filtrate add a solution of acetate of sodium (App. § 27), drop by drop, until the mixture smells of acetic acid; a red or brownish-red precipitate of arseniate of silver appears. The acetate of sodium is added because the arseniate of silver is soluble in nitric acid, and but sparingly soluble in acetic acid, unless it is present in considerable excess. On the addition of acetate of sodium to the liquid containing free nitric acid, there was formed nitrate of sodium, and acetic acid was set free.

Any precipitate supposed to contain arsenic may be further examined by converting the arsenic into a hydrogen compound by the method known as Marsh's test. (See Elic and Storer's *Manual of Inorganic Chemistry*, pp. 259, 270; see also the test for antimony below.) This method is applicable to the detection of very minute quantities of arsenic.

The insoluble residue containing antimony and tin, which was left on the filter, is washed several times with a mixture of equal parts of alcohol and water, and then transferred to a test-tube or porcelain dish and warmed with strong chlorhydric acid. Choose a cork or caoutchouc stopper provided with two holes, which fits accurately the mouth of a wide test-tube. Fit a small thistle-tube to one of the holes, and to the other a short bent tube drawn to a rather fine open point. Put a fragment or small strip of zinc (App., § 56), together with a bit of platinum foil into the tube, cover with water, close the tube with the perforated stopper and, through the thistle-tube add strong chlorhydric acid in small

successive portions. After hydrogen has been generated freely during four or five minutes by the mixture in the tube, and all the air originally contained in the latter has been expelled, light the gas issuing from the pointed glass tube, and pour into the thistle-tube, a portion at a time, the mixture of strong chlorhydric acid and the residue containing antimony and tin, or the solution if the acid has dissolved the residue completely. Hold a cold porcelain dish in the flame, taking care to shift the position of the dish frequently so that fresh surfaces of porcelain may be exposed to the burning gas. If there be really any antimony in the insoluble residue, antimoniucretted hydrogen will be evolved, together with free hydrogen, and characteristic smoky-black spots or stains of metallic antimony will be deposited from it upon the cold porcelain. To be sure that the spots are really composed of antimony and not of arsenic, cover them with a solution of bleaching powder (hypochlorite of calcium); if they are antimony spots they will not dissolve, while arsenic spots dissolve at once. (Compare Eliot and Storer's Manual, pp. 270, 271.)

Test
for
Sb.

In order not to explode the test-tube on lighting the gas, the operator must wait patiently for several minutes, until all the air has been expelled from the tube.

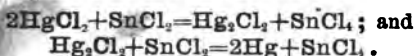
The whole of the antimony is not converted by this means into antimoniucretted hydrogen; a portion is reduced to the metallic state, and if the evolution has not been too rapid, will be found deposited on the platinum foil as a firmly adherent dark coating or stain. Therefore when the zinc in the test-tube is all or nearly all consumed, transfer the contents of the tube to a porcelain dish and examine the platinum foil for this indication of the presence of antimony.

In the operation just performed, the tin which existed as oxide has been converted into the metallic state, and now awaits examination in the porcelain dish. Remove and rinse any zinc remaining undissolved and carefully decant from the dark spongy mass in the dish, the solution with which it is

covered and which consists mainly of chloride of zinc. The residue is warmed with strong chlorhydric acid, in which the tin dissolves. Pour off the solution of stannous chloride

Test thus obtained; and add to it two or three drops of
for a solution of mercuric chloride (corrosive sublimate)

Sn. (App., § 54). A white or gray precipitate of mercurous chloride (calomel), often mixed with gray metallic mercury will be thrown down, for:—



To prove that the precipitate really contains calomel, decant the supernatant liquid, cover the precipitate with ammonia-water, and heat the mixture to boiling (compare p. 18).

26. An outline of the foregoing operations may be represented in tabular form as follows:—

The General Reagent (H_2S) of Class III precipitates As_2S_3 , Sb_2S_3 , and SnS or SnS_2 , [Au_2S_3 and [PtS_2]]. (As well as the members of Class II, from which Class III is separated by solution in sulphhydrate of sodium.) The sulphhydrate of sodium solution is treated with nitric acid and nitrate of sodium, and the mixture evaporated and heated to fusion. The fused mass is treated with cold water:—

Arseniate of sodium (with nitrate of sodium, etc.) goes into solution. Confirm presence of As by magnesium mixture and by the silver test.	Antimoniate of sodium and oxide of tin remain undissolved. Reduce with zinc and HCl in presence of platinum foil.
	Antimoniuiretted hydrogen is formed and antimony spots obtained. Tin is left in the metallic state (together with some antimony which stains the foil). Dissolve the tin in HCl and test with HgCl₂ .

In the case of mixtures containing gold and platinum (see § 13), as well as arsenic, antimony and tin, the gold and platinum would remain with the tin, without interfering in any way with the separation or detection of either member of the

class, and when the tin reduced by zinc is dissolved in chlorhydric acid, the gold and platinum would remain undissolved (together with some antimony, if present). Since the sulphides of gold and platinum are both black, while those of arsenic and tin are yellow or brown, and that of antimony is orange, the presence of any considerable quantity of either of the precious metals would be indicated by the black color of the class precipitate.

There are excellent special tests both for gold and for platinum, by which these elements may be detected even in the presence of all the other metals. Hence it is most convenient to make special search for them in the original substance, by methods to be described hereafter (§ 96, b.), whenever the preliminary examination has given reason to suspect the presence of either of them.

27. The method of separating Class II from Class III has been sufficiently described in §§ 8, 24. When members of Class II are altogether absent, something may be learned from the color of the precipitate produced by sulphuretted hydrogen. Thus, —

An orange colored precipitate indicates the presence of antimony ;

A bright yellow precipitate, the presence of arsenic ;

A dull yellow precipitate, white at first, the presence of bisulphide of tin (stannic sulphide).

A dark brown precipitate, the presence of protosulphide of tin (stannous sulphide).

A black precipitate the presence of gold or platinum.

When, as a result of the preliminary examination (§ 80, III, c), there is reason to suspect the presence of mercury as a mercuric salt, sulphhydrate of ammonium which has become somewhat yellow from standing, should be substituted for sulphhydrate of sodium, because sulphide of mercury is rather soluble in sulphhydrate of sodium. In the event of the analysis of an unknown solution, if on the treatment with nitric acid of the solution of sulphides in sulphhydrate of so-

tated in combination with members of Class IV, in the form of chromite, ferrite or aluminate of manganese. The general scheme for the examination of Class IV, necessarily provides for the detection of all the members of the class in the possible presence of these extraneous substances.

29. Example of the Precipitation with Ammonia-water.—Pour into a beaker a small teaspoonful of aqueous solutions (App., § 62) of sulphate of manganese, common alum (sulphate of aluminum and ammonium), chrome alum (sulphate of chromium and potassium), and chloride of iron (ferrous chloride). As an example of the substances insoluble in water which might be present in an acid solution, dissolve in a small amount of boiling chlorhydric acid, a not very large quantity, say half a gramme, of bone-ash (phosphate of calcium), and add the solution to those already placed in the beaker. Fill the beaker about one third full of water, heat the mixture to boiling and add to it two or three drops of strong nitric acid to convert the iron into ferric salts. Boil the mixture for a minute or two and then add, little by little, ammonia-water to the boiling liquor until a distinct odor of ammonia is perceptible after the mixture has been thoroughly stirred.

30. Analysis of the Mixed Precipitate.—The following method of detecting iron, chromium, aluminum (and manganese) in the mixed precipitate which may contain all of them, together with phosphates and other compounds of barium, strontium, calcium and magnesium, depends:—1st. Upon the oxidation and conversion of the hydrates of manganese and chromium into manganate and chromate of sodium (or potassium) when fused with a mixture of carbonate of sodium and nitrate of potassium; while the hydrate of aluminum under the same treatment is converted, to a greater or less extent, into aluminate of sodium, and the compounds of barium, strontium and calcium either remain unchanged or are converted into carbonates. 2d. Upon the solubility of the chromate and aluminate of sodium (or potassium) in water

and the insolubility of the carbonates or other compounds of barium, strontium and calcium which may be present in the fused mass. 3d. Upon the sparing solubility of chromate of lead in acetic acid. 4th. Upon the peculiar green color of the manganate of sodium (or potassium). 5th. Upon the fact that Prussian blue is formed when a solution of ferrocyanide of potassium is added to the solution of a ferric salt. 6th. Upon the sparing solubility of the oxalates of barium, strontium and calcium in dilute acetic acid.

The details of the treatment of the precipitate produced by ammonia-water, are as follows:—Collect the precipitate upon a filter, wash it two or three times with water, and then dry it either on the filter or by transferring it to a piece of platinum foil or to a platinum crucible (App., § 80) and heating over the lamp gently so as to avoid spattering. The dry precipitate is mixed intimately (best by rubbing in a mortar) with five or six times its bulk of a dry mixture of equal parts of carbonate of sodium and nitrate of potassium (App., § 36). The mixture is then fused thoroughly by heating it over the lamp either on platinum foil or in a platinum crucible. If the amount of the mixture be small, a piece of foil answers very well; larger quantities may be fused in successive portions on the foil, but a small crucible is much more convenient.

If only a manganese compound and no chromium had been fused on the foil, the cold mass would have exhibited the peculiar bluish-green color of manganate of sodium (or potassium) owing to the oxidation of a small portion of the hydrate of manganese to manganic acid in the presence of carbonate of sodium and nitrate of potassium. If only chromium had been present, the bright yellow color of chromate of sodium (or potassium) would have been clearly perceived. But from mixtures of the manganate and chromate of sodium, (or potassium) in various proportions, different shades of green, brownish-green or yellowish-green, will result. When iron is present, the red color of its oxide may obscure the colors due to manganese and chromium.

Place the platinum foil or crucible in a porcelain dish, cover it with water, and boil the latter until all the soluble matter has been dissolved from the foil. Take out the foil, rinse it, and throw the contents of the dish upon a filter. The manganate, chromate and aluminate of sodium pass into the filtrate, along with the excess of the carbonate of sodium and nitrate of potassium employed: the filtrate is colored yellow by the chromate. The insoluble residue, in this case, consists of the oxides of iron and manganese, together with the phosphate of calcium which has not been altered by the fusion, and any small portion of carbonate of calcium which may have been formed by the decomposition of a part of the phosphate. In the case of an actual analysis there might be also phosphates, carbonates and other insoluble compounds of barium, strontium and magnesium.

Divide the filtrate from the insoluble residue of the fusion into two portions. Carefully add acetic acid, drop by drop, to one of these portions until the liquor exhibits an acid reaction, and then add to it two or three drops of a solution of acetate of lead (App., § 45). An insoluble precipitate of chromate of lead will be immediately thrown down, exhibiting a bright yellow color if the reagents be all pure. But if, as often happens, the carbonate of sodium, employed as the
 Test flux, is contaminated with sulphate of sodium, the
 for yellow color of the precipitate will tend towards
 Cr. white, in proportion to the amount of sulphate of lead which has gone down together with the chromate. A pure white precipitate would be no indication of chromium, but only of a sulphate in the reagents.

Acidulate the other portion of the aqueous solution of the fused sodium (and potassium) compounds with dilute chlor-
 Test hydric acid, add ammonia-water to slight alkaline
 for reaction, warm the mixture and leave it at rest for
 AL at least half an hour or, better, over night. After the lapse of some time, a characteristic, gelatinous, colorless agglomeration of particles of hydrate of aluminum will appear at the top or bottom of the liquid.

It should be said, that flocks of hydrate of aluminum, when diffused through a liquid, are almost transparent enough to elude observation. When an acid solution, containing much aluminum, is mixed with ammonia-water and warmed, a copious precipitate of hydrate of aluminum will appear immediately, and will often remain floating for some time upon the surface of the solution by virtue of bubbles of air entangled in it. But since it is not easy to convert the whole of the alumina in the original precipitate into soluble aluminate of sodium, by fusion with carbonate of sodium in the method above described, the quantity of the hydrate to be thrown down at the final test is often very small, and considerable time must be allowed, in order that every particle of it may separate from the solution, and all the particles collect into a single mass.

To confirm the presence of aluminum, collect the hydrate in the point of a small filter and allow it to drain. Cut away the superfluous paper, place that portion of the filter to which the precipitate is attached upon a piece of charcoal, and heat it intensely in the blowpipe flame. Moisten the residue with a drop of a solution of nitrate of cobalt and again ignite it strongly. The unfused compound of aluminum, cobalt and oxygen left upon the coal will exhibit a deep sky-blue color when allowed to cool. This reaction is useful in distinguishing the hydrate of aluminum from that of glucinum, an element somewhat similar to aluminum though far less abundant. Hydrate of glucinum when ignited with nitrate of cobalt does not yield a pure blue compound, but only a gray mass.

Return now to the insoluble residue of the fusion with carbonate of sodium and nitrate of potassium. If the characteristic color of the manganate of sodium (or potassium) were not distinctly observed at the previous fusion, take a small quantity of the insoluble residue and fuse it with twice its bulk of a mixture of carbonate of sodium and nitrate of potassium upon platinum foil in a strong *oxidizing*

blowpipe flame (App., § 78). The peculiar bluish-green

Test coloration of manganate of sodium will appear in
for the fused mass, as soon as it has become cold, par-
Mn. ticularly at the edges and thinner portions. In thus
 testing for manganese, it is well to incline the foil, so that por-
 tions of the thoroughly melted mass may flow away from the
 centre of the mixture into thin sheets, in order that the color
 of the manganate may be exhibited in its purity.

Boil a second small portion of the insoluble residue with a
 little strong chlorhydric acid, dilute the solution with water,
 and add a drop or two of ferrocyanide of potassium. The
 liquid will immediately become colored with Prussian blue,

Test an indication of the presence of iron. In case much
for iron be present, the blue color may be too deep to
Fe. be recognized until the liquid has been diluted with
 a large quantity of water.

Warm another portion of the insoluble residue with a few
 drops of acetic acid, dilute the solution with water and filter
 if anything remain undissolved. To the slightly acid liquid
 add a teaspoonful of a solution of oxalate of ammonium
 (App., § 20). Any compounds of barium, strontium and
 calcium which may have been present in the residue will be
 deposited as oxalates, as the oxalates of these elements are
 but sparingly soluble in acetic acid. In the present case there
 will be a precipitate of oxalate of calcium. Allow the mix-
 ture to stand for some time and finally collect the precipitate
 on a filter, wash, dry and preserve for future examination in
 connection with Class VI.

In addition to the elements present in the solution which
 has just been analyzed, compounds of magnesium are also
 under certain circumstances precipitated with the hydrates
 of Class IV. In actual practice, therefore, the remainder of
 the insoluble residue is examined for magnesium, as follows:—
 Heat the mixture strongly on the platinum-foil so as to ren-
 der the oxides of aluminum and iron as insoluble as pos-
 sible, and then treat with dilute chlorhydric acid and warm

gently. Without regarding the matter which remains undissolved add to the mixture (which contains in solution, along with the magnesium, some iron, aluminum, calcium, etc.) a teaspoonful of chloride of ammonium, and ammonia-water to alkaline reaction. Throw the mixture upon a filter, collect the filtrate, and add it to that originally obtained from the precipitate of Class IV: this mixed filtrate will be examined in due course (Class VII) for magnesium. In case the whole amount of the residue from the fusion of the precipitate of the class with carbonate of sodium and nitrate of potassium, be but small, it is well to filter the liquid of the preceding paragraph which contains the precipitated oxalates of barium, strontium and calcium, to evaporate the filtrate to dryness and ignite to destroy the oxalic and acetic acids. The residue is subsequently treated with chlorhydric acid, chloride of ammonium and ammonia, filtered and the filtrate added to the filtrate from the original Class IV precipitate.

31. An outline of the foregoing operations may be tabulated as follows:—

<p>The General Reagent ($[\text{NH}_4]_2\text{HO}$ mixed with NH_4Cl) of Class IV precipitates the hydrates of Fe, Cr and Al together with Mn (as a chromite, ferrite or aluminite), and various phosphates and other compounds of Fe, Cr, Al, Ba, Sr, Ca and Mg. The precipitate is dried and fused with Na_2CO_3 and KNO_3; the fused mass is treated with water and filtered:—</p>					
Divide the filtrate into two portions:—			Divide the precipitate into four portions:—		
Yellow color of the solution indicates Cr . Confirm Cr by precipitation of PbCrO_4 .	Acidulate with HCl and add $(\text{NH}_4)_2\text{HO}$:— Colorless flocculent precipitate proves presence of Al .	Test for Mn by fusing with Na_2CO_3 and KNO_3 .	Test for Fe with ferrocyanide of potassium.	Test for Ca, etc. by precipitation of the oxalates from acetic acid solution.	Eliminate Mg by dissolving in HCl and reprecipitating Class IV with NH_4HO

In the actual examination of an unknown substance, the analysis is somewhat simplified, if the substance be a solid soluble in water, or if it be a neutral solution, or if by any other means we know that the phosphates, oxalates, etc., mentioned above are absent. The treatment in such a case may be simplified by the omission of those operations looking to the separation of calcium, barium, etc., from the residue of the fusion with carbonate of sodium and nitrate of potassium.

To determine whether the iron in the substance subjected to analysis was originally in the state of a ferric or a ferrous salt, test a small quantity of the original solution with a drop of ferricyanide of potassium (App., § 34). The formation of Prussian blue proves the presence of a ferrous salt. Another small portion of the original solution, tested with a drop of a ferrocyanide of potassium, would yield Prussian blue in case the solution contained a ferric salt. In applying either of these tests, the blue coloration, indicative of iron, is alone to be looked for; no notice need be taken of other colorations, or of precipitates formed by the action of the ferri- or ferro-cyanide upon the various metallic salts which the solution may contain. The possibility that a ferrous salt may have been changed into a ferric during the process of getting the original substance, if a solid, into solution, must not be lost sight of.

32. Separation of Class IV from Class III. The methods of eliminating Classes I, II and III from mixtures which contain members of these classes as well as of Class IV, have already been described in §§ 6 and 8.

It is essential to the success of the operation that all the sulphuretted hydrogen in the filtrate from Classes II and III be expelled, for sulphuretted hydrogen precipitates all the members of Classes IV and V from alkaline solutions, and the filtrate now in question is, of course, made alkaline when ammonia-water is added to it. The conversion of the iron into a ferric salt (by means of nitric acid) is necessary because ferrous hydrate is somewhat soluble in ammonium-salts,

and could not, therefore, be precipitated completely by ammonia-water in the acid filtrate from Classes II and III.

No matter what the condition of the iron may have been in the original solution, it is reduced to the state of ferrous salts by sulphuretted hydrogen. The filtrate from the precipitate produced by sulphuretted hydrogen (the general reagent of Classes II and III) should, therefore, be placed in a porcelain dish, and boiled, until the steam from it ceases to blacken lead paper. After the sulphuretted hydrogen has been expelled, three or four drops of strong nitric acid must be added to the liquid, and the mixture boiled for a moment longer to convert the iron into ferric salts. If by accident the student should fail to convert the iron entirely to the state of a ferric salt, there will be produced a greenish, slimy precipitate of ferrous hydrate on the addition of the ammonia-water. Such a precipitate must not be confounded with the green hydrate of chromium: it should be redissolved in nitric acid and the acid solution boiled anew for a few minutes before reprecipitating with ammonia-water.

When all the iron has been converted in the state of a ferric salt, a small quantity of a solution of chloride of ammonium is added to the boiling liquid, and finally ammonia-water, little by little, with constant stirring, until a persistent odor of ammonia is perceptible. A large excess of ammonia must be carefully avoided, for hydrate of aluminum, being somewhat soluble in ammonia-water, might be kept in solution, to the disturbance of the analysis of Classes VI and VII.

It will be remembered that the object of using chloride of ammonium is to hold in solution magnesium (of Class VII) and the members of Class V. This it does in virtue of the fact that the double salts formed by the union of ammonium compounds with compounds of the elements in question are soluble in water and also in ammonia-water. A considerable quantity of the ammonium salt will, of course, be formed in any event by the action of the ammonia-water upon the

chlorhydric acid in the solution, but it is best always to add a further portion of the chloride as a precautionary measure.

The following inferences may be drawn from the color of the precipitate produced by ammonia-water: —

A gelatinous, white precipitate indicates aluminum or some one of the oxalates, phosphates, etc., mentioned above.

A grayish-green or grayish-blue precipitate indicates chromium.

A reddish-brown precipitate indicates iron.

If no precipitate is produced by the ammonia-water, all the members of Class IV are absent, and the solution may at once be tested with sulphhydrate of ammonium, the general reagent of Class V.

When the solution contains much chromium, a small portion of this element is apt to remain dissolved at first in the excess of ammonia-water, and to color the solution pink; but by continuing to boil the solution, the color may be made to disappear, and the whole of the chromium may be thrown down. Care must be taken to replace, by small portions, the water driven off by boiling, lest some of the members of Class V be converted into insoluble compounds.

It is to be observed that the legitimate members of Class IV cannot be completely precipitated by ammonia-water from solutions which contain non-volatile organic substances, like albumin, sugar, starch, and so forth, or organic acids (such as tartaric, citric, oxalic, or even in some cases acetic acid) which form soluble double salts by uniting simultaneously with the ammonium and one or more of the members of the class. The treatment of substances containing organic matter will be explained hereafter. (§ 82.)

CHAPTER VI.

CLASS V.—ELEMENTS WHOSE SULPHIDES ARE INSOLUBLE IN WATER AND IN SALINE OR ALKALINE SOLUTIONS.

33. Example of the Precipitation of the Members of Class V.—Place in a small glass flask a half teaspoonful of aqueous solutions (App., § 62) of the sulphates, nitrates, or chlorides of cobalt, nickel, manganese and zinc. Add to the mixture five or six teaspoonfuls of a solution of chloride of ammonium, as much water, and ammonia-water to alkaline reaction.

Heat the mixture to boiling, and add sulphhydrate of ammonium to the boiling solution, drop by drop, with frequent agitation, as long as a precipitate continues to be formed. (Compare p. 12.) In the present case there are special reasons why the precipitate should be boiled and shaken, in order to make it compact; for the sulphides of Class V, when loose and flocculent, are not only easily acted upon by the air and by dilute acids, but are peculiarly liable to pass through the pores of filter-paper, and yield muddy filtrates.

At the best, these sulphides oxidize rapidly when moist, with formation of soluble sulphates which are liable to pass through the filters and contaminate the filtrates. The analysis of the sulphides should therefore be proceeded with immediately after the precipitation with sulphhydrate of ammonium, and should be conducted in such manner that no precipitate of a sulphide shall ever be left moist upon a filter more than half an hour.

34. Analysis of the Mixed Sulphides.—The detection of the several members of Class V depends:—1st. Upon the almost complete insolubility of the sulphides of cobalt

and nickel in cold dilute chlorhydric acid, and the ready solubility of the sulphides of manganese and zinc in that liquid. 2d. Upon the solubility of hydrate of zinc, and the insolubility of hydrate of manganese, in a solution of caustic soda. 3d. Upon the insolubility of sulphide of zinc in acetic acid, in presence of sulphuretted hydrogen. 4th. Upon the peculiar colors imparted to borax glass by compounds of cobalt and nickel dissolved in the glass; and upon certain other special tests to be described directly.

To effect the separation:—Collect the precipitate upon a filter, and rinse it once or twice with water; spread open the filter in a porcelain dish, and cover it with cold dilute chlorhydric acid. Scarcely any of the sulphide of cobalt, or of nickel, will go into solution, while the sulphides of manganese and zinc will be completely decomposed, and dissolved as chlorides.

Filter the chlorhydric acid solution, pour the filtrate into a porcelain dish, and boil it until strips of moistened lead paper held in the steam no longer indicate the presence of sulphuretted hydrogen; then add caustic soda to the liquid in slight excess. A whitish gelatinous precipitate of hydrate of manganese, insoluble in caustic soda, will be thrown down, together with small portions of the hydrates of cobalt and nickel, resulting from the partial decomposition of the sulphides of these metals by the chlorhydric acid, while the hydrate of zinc at first precipitated redissolves completely in the excess of soda. It is to be observed that precipitation should never be effected in a porcelain dish, since a white or transparent precipitate is scarcely visible in a white and opaque dish.

To prove the presence of manganese, collect the precipitate upon a filter, allow it to drain, and fuse a small portion of it
 Test with a mixture of carbonate of sodium and nitrate
 for of potassium upon platinum foil in the oxidizing
 Mn. blowpipe flame, as directed on p. 42.

Acidify the alkaline filtrate with acetic acid; then pass sul-

phuretted hydrogen into the liquid. Sulphide of zinc will be thrown down as white or dirty white flocculent precipitate.

To confirm the presence of zinc: — Collect the precipitate produced by sulphuretted hydrogen upon a filter and allow to drain; transfer it to a porcelain dish, dissolve it in dilute chlorhydric acid, and evaporate the solution almost to dryness on a water-bath (App., § 77). Dissolve the residue in a few drops of water, and without heeding the milkiness which the presence of particles of free sulphur may produce in it, pour this liquid into a test-tube containing two or three teaspoonfuls of a solution of normal chromate of potassium previously heated to boiling. A peculiar, yellow, somewhat flocculent precipitate of basic chromate of zinc will form in the boiling liquid, and will soon subside to the bottom of the tube. The red color of the supernatant fluid is due to the formation of bichromate of potassium.

Test
for
Zn.

It is to be observed that in the analysis of mixtures which contain no manganese, the precipitate of hydrate of cobalt or of nickel, produced by the caustic soda, is usually small and sometimes hardly perceptible; but, no matter how minute the precipitate may be, it must always be carefully removed by filtration before testing the solution for zinc with sulphuretted hydrogen.

The black residue, insoluble in dilute chlorhydric acid, is washed with water and tested for cobalt and nickel, by heating successive small portions of it in a bead (§ 89, c.) of borax (App., § 25) in the oxidizing blowpipe flame. If cobalt alone were present, a bright, pure blue color would be imparted to the bead. On the other hand, if the precipitate was composed solely of sulphide of nickel, the borax glass would assume a peculiar reddish-brown color. Mixtures of the two sulphides yield beads of various tints, according to the proportions of nickel and cobalt contained in them. By adding the precipitate to the borax by repeated small portions, and fusing the bead anew after each addition, it is often possible to obtain first the characteristic color of

Tests
for
Co&Ni.

If the precipitate of zinc is white, it is a good test that no Co or Ni is present. If all does not clear in the HCl it is probably Zn white.

one of the elements, and afterwards tolerably well defined indications of the other.

The blue color of cobalt can usually be made manifest, even in presence of much nickel, by heating the borax bead in the reducing blowpipe flame (App., § 78). In the reducing flame the reddish-brown color imparted by nickel changes to gray, while the cobalt blue remains unaltered.

In any event, one of the two metals will be detected by the blowpipe test, and the subsequent operations can be limited to searching for the other.

To prove the presence of nickel, boil the black residue with a few drops of aqua regia in the porcelain dish, and evaporate the solution almost, but not quite, to dryness. Add to the residual acid liquor, little by little, a strong solution of cyanide of potassium, until the reaction of the solution becomes decidedly alkaline; the cyanides of nickel and cobalt at first thrown down both redissolved easily in an excess of cyanide of potassium. Boil the mixture for several minutes, adding water by small portions to replace that lost by evaporation. Then add a solution of hypochlorite of sodium until the liquid, after shaking, smells strongly of it, and boil again. The nickel is precipitated as black hydrated peroxide (nickelic hydrate, $\text{Ni}_2\text{H}_2\text{O}_6$), while the compound of cobalt in solution (cobalticyanide of potassium) is not affected. If a light-colored precipitate appears, it may indicate that an insufficient quantity of hypochlorite of sodium has been added, and in the case of a solution actually under examination more of the reagent should be added before pronouncing nickel absent.

To confirm the presence of cobalt in case of doubt:—dissolve the black residue in a few drops of hot aqua regia, evaporate the solution nearly to dryness, pour into the residual solution two or three times its own volume of a solution of nitrite of potassium (App., § 37), and add to the mixture concentrated acetic acid, until the reaction of the liquid is strongly acid.

Transfer the mixture to a test-tube, and leave it at rest during eighteen or twenty-four hours. A beautiful, yellow crystalline precipitate of the double nitrite of cobalt and potassium will be deposited sooner or later, according to the proportion of cobalt which the solution contained.

Test
for
Co.

On adding caustic soda to the filtrate from the cobalt precipitate, hydrate of nickel would be thrown down if present, and the presence of nickel might be confirmed by testing this precipitate with borax in the oxidizing blowpipe flame.

35. An outline of the foregoing operations may be tabulated as follows:—

The General Reagent ($[\text{NH}_4]\text{HS}$) of Class V precipitates CoS , NiS , MnS and ZnS . Treat the precipitate with dilute HCl :—		
CoS and NiS remain undissolved.	MnCl_2 and ZnCl_2 go into solution. Boil, to expel H_2S , and add NaHO :—	
Test for Co and Ni with borax glass and, if need be, with NaClO or KNO_3 .	Hydrate of manganese is precipitated, together with traces of the hydrates of Co and Ni . Prove presence of Mn by the blowpipe test.	Hydrate of zinc goes into solution. Add H_2S to throw down ZnS . Confirm presence of Zn by precipitation of the chromate.

36. Separation of Class V from Class IV.—After Classes I, II, III and IV have been removed in the manner already described (§§ 9, 32), add a single drop of sulphhydrate of ammonium of good quality (App., § 17) to the filtrate from Class IV. If no precipitate is produced, none of the members of Class V can be present, and the solution may be immediately tested with carbonate of ammonium, the general reagent of Class VI.

If the first drop of the sulphhydrate produces a precipitate, transfer the mixture to a small flask, heat it until it actually boils and add more of the sulphhydrate, with the precautions enjoined on p. 12 to complete the precipitation.

In case the precipitate produced by sulphhydrate of ammonium is white, the presence of zinc is indicated.

If it be flesh-colored, or yellowish-white, and becomes brown by oxidation when exposed to the air, the presence of manganese is to be inferred.

In case the precipitate is black, either cobalt or nickel, or both these elements, are present. Both of them must be sought for, whenever the precipitate exhibits any tinge of black at the moment of its formation.

As the sulphide of nickel is not absolutely insoluble in sulphhydrate of ammonium, it not infrequently happens that the filtrate from Class V is dark-colored, owing to the presence of sulphide of nickel in solution. In such case it is well to acidify the liquid with chlorhydric acid, and to collect the dark-colored precipitate (which consists of sulphide of nickel mixed with free sulphur) on a filter, and to test for nickel by means of the borax bead. The filtrate must then be made alkaline with ammonia-water before testing for Class VI.

CHAPTER VII.

CLASS VI.—ELEMENTS WHOSE CARBONATES ARE INSOLUBLE IN WATER, AMMONIA-WATER AND SALINE SOLUTIONS.

37. Example of the Precipitation of the Members of Class VI. — Place in a small beaker a teaspoonful of aqueous solutions of the chlorides or nitrates of barium, strontium and calcium. Add to the mixture two or three teaspoonfuls of a solution of chloride of ammonium, enough ammonia-water to produce an alkaline reaction, and finally a solution of carbonate of ammonium, drop by drop, as long as any precipitate continues to be produced by fresh portions of this reagent. To determine this last point, heat the mixture to boiling at intervals, and after boiling allow it to settle, until a sufficient quantity of comparatively clear liquid has collected at the top of the mixture to permit the application of the test.

38. Analysis of the Mixed Carbonates. — The separation of barium, strontium and calcium, one from the other, depends: — 1st. Upon the insolubility of chromate of barium in dilute acetic acid, and the solubility of the chromates of strontium and calcium in that liquid. 2d. Upon the fact that sulphate of strontium is almost absolutely insoluble in acidulated water, while sulphate of calcium, though rather sparingly soluble in water, is still sufficiently soluble to be kept in solution. (See App., § 30.)

Collect the precipitate upon a filter, wash it two or three times with water, taking care to collect the precipitate at the apex of the filter, and dissolve it in acetic acid. The acid may be poured into the filter as it rests in the funnel, but

only a few drops should be used, and the filtrate should be poured back repeatedly upon the filter, until all the precipitate has been dissolved. If the portion of acid at first taken becomes saturated before the precipitate is entirely dissolved, it will be necessary to add an additional small amount. Finally rinse the filter with a little water from a wash-bottle with small orifice, collect the wash-water with the filtrate, and shake the mixture.

Pour a small portion of the acetic acid solution into a test-tube, and add to it a drop of a solution of normal chromate of potassium. A pale yellow precipitate falls when barium is present, as in this instance; for chromate of barium is well-

Test high insoluble in acetic acid, especially in presence
for of saline solutions. In order to separate the whole

Ba. of the barium, pour the contents of the test-tube into the reserved portion of the acetic acid solution, heat the mixture to boiling, and add to it chromate of potassium, until no more precipitate falls and the supernatant liquor appears distinctly yellow, after having been well shaken and allowed to settle. Filter the mixture, and proceed to examine the filtrate for strontium and calcium.

If no barium had been present, no precipitate would have been produced by chromate of potassium in the small portion of liquid first tested, and it would have been unnecessary to mix this reagent with the rest of the acetic acid solution. Trouble would thus be saved, as will appear below.

It sometimes happens that chromate of barium is precipitated in the form of powder so fine that some particles of it pass through the pores of the paper and contaminate the filtrate. Now, in order to detect strontium and calcium it is absolutely necessary that this filtrate, although of a bright yellow color, should be perfectly transparent and free from suspended particles of the barium salt. If then the filtrate is at all turbid, it must be poured back repeatedly into the and again collected in clean tubes, until the last trace of cloudiness has disappeared.

To the filtrate from the chromate of barium add ammonia-water to alkaline reaction, and carbonate of ammonium as long as a precipitate falls. Heat the mixture to boiling for a moment, collect the precipitate upon a small filter, and wash it with water, until all the chromate of potassium has been removed, and the wash-water runs colorless from the filter.

Dissolve the precipitate in the smallest possible quantity of acetic acid, and mix it with three or four times its volume of a solution of sulphate of potassium (App., § 30), made of such strength that, though capable of throwing down sulphate of strontium, it cannot precipitate sulphate of calcium. Allow the mixture to stand at rest for two hours or more, in order that the white powder of sulphate of strontium Tests may separate completely. Then filter, and to the for filtrate add ammonia-water to alkaline reaction, and **Sr&Ca.** half a teaspoonful of a solution of oxalate of ammonium. A white precipitate of oxalate of calcium will be immediately thrown down.

Since sulphate of strontium is somewhat soluble in a solution of chromate of potassium, the filtrate from chromate of barium cannot be examined directly for strontium by means of sulphate of potassium. The strontium and calcium are consequently reprecipitated as carbonates, in order that the excess of chromate of potassium may be washed away. The operation serves also to collect the strontium and calcium out of the mass of liquid in which they have become diffused, and to concentrate them to a small bulk.

It should be observed that, when the proportion of strontium or calcium in a mixture is small, it often happens that the precipitate, produced by carbonate of ammonium in the filtrate from chromate of barium, is held in suspension and concealed so completely in the yellow liquor, that an unpractised eye can hardly detect the fact that the liquid has become cloudy. That a precipitate has really been formed in such cases is easily discovered by throwing a portion of the mixture upon a filter, and comparing the clear filtrate thus ob-

tained with that portion of the mixture which has been left unfiltered.

39. An outline of the foregoing operations may be presented in tabular form, as follows:—

The General Reagent, $[\text{NH}_4]_2\text{CO}_3$, of Class VI precipitates the carbonates of Ba, Sr and Ca. Dissolve in dilute acetic acid, and add K_2CrO_4 :—		
BaCrO ₄ is thrown down as a yellow powder.	Sr and Ca remain in solution. Add $(\text{NH}_4)\text{HO}$ and $(\text{NH}_4)_2\text{CO}_3$. Collect and wash the precipitate, and dissolve it in acetic acid. Add dilute K_2SO_4 :—	
	SrSO ₄ is thrown down.	Ca remains in solution. Add oxalate of ammonium, to precipitate the calcium as oxalate.

40. Separation of Class VI from the Preceding Classes. — After Classes I, II, III, IV and V have been separated in the manner already described (§§ 6 to 10), there will still always remain to be examined the filtrate from Class V, and sometimes a precipitate (§ 30) composed of oxalates of barium, strontium, calcium (and magnesium), — in case any salt of these elements, insoluble in ammonia-water, has been thrown down with the members of Class IV.

If such a precipitate has been obtained in the analysis of Class IV, the oxalic acid contained in it must now be destroyed, the remainder of the precipitate brought into solution, and this solution added to the filtrate from Class V, before proceeding to precipitate the members of Class VI. To this end, ignite the dry precipitate carefully upon platinum foil,—by several successive portions if the precipitate is large,—taking care that none of the powder is left sticking to the paper or lost by dropping it from the foil. At a moderate heat the oxalates suffer decomposition, and only carbonates or oxides are left upon the foil. Place the foil and the residue in a small porcelain dish, and dissolve the residue in boiling dilute chlorhydric acid. Add a few drops of chloride of am-

monium to the solution, neutralize the acid with ammonia-water, pour the liquid upon a small filter and add the filtrate to that obtained from Class V. Then add a solution of carbonate of ammonium to the mixture, and boil it in the manner described in § 37.

If there be no precipitate of the oxalates from Class IV, the filtrate from Class V will, of course, be treated directly with carbonate of ammonium, care being taken to add only a drop or two of the reagent, at first, to ascertain whether any of the members of Class VI are really contained in the solution.

The solution to which the general reagent carbonate of ammonium is added, must contain chloride of ammonium, to prevent the precipitation of magnesium as a carbonate, and also ammonia-water, to hinder the decomposition of the carbonates of barium, strontium and calcium by the boiling chloride of ammonium. But since the excess of ammonia-water and the chloride of ammonium, added to the solution before the separation of Class IV, are still contained in it, no new quantity of either of them need here be added.

It is to be remembered, in this connection, that the carbonates of barium, strontium and calcium are all slightly soluble in a solution of chloride of ammonium, and that no precipitate whatever is produced when carbonate of ammonium is added to a weak solution of either of the members of Class VI, in case a large quantity of chloride of ammonium has been previously mixed with it. On this account it is well in an actual analysis to concentrate by evaporation the filtrate from the Class V precipitate before adding the carbonate of ammonium solution, and in some cases, where a very large amount of ammonium salts is present, it is well to evaporate to complete dryness and then to ignite in order to drive off the ammonium compounds. The residue when cold is dissolved in a small quantity of chlorhydric acid; two or three teaspoonfuls of a solution of chloride of ammonium are added, then ammonia-water, and, finally, carbonate of ammonium, as in § 37.

In a solution containing traces of barium or strontium these elements might fail to be detected, in case the chlorhydric acid employed in the process of separating Classes I and II was contaminated with sulphuric acid, or in case the original liquid contained nitric acid to oxidize a portion of the sulphur of the sulphuretted hydrogen employed to precipitate Class II, or even if the nitric acid, employed to oxidize iron in the filtrate from Classes II and III, were added before the sulphuretted hydrogen had been expelled. All danger is avoided, however, by using pure chlorhydric acid to precipitate Class I, and expelling the nitric acid from the filtrate by evaporating the latter to dryness upon a water-bath, covering the residue with pure concentrated chlorhydric acid, again evaporating until the mixture becomes dry, and finally dissolving in water acidulated with chlorhydric acid.

CHAPTER VIII.

CLASS VII.—INCLUDES THE REMAINING COMMON ELEMENTS NOT COMPRISED IN THE PRECEDING CLASSES, NAMELY: MAGNESIUM, SODIUM AND POTASSIUM.

41. The Detection of the Several Members of Class VII depends:— 1st. Upon the insolubility of a double phosphate of magnesium and ammonium, and the solubility of the phosphates of potassium and of sodium; and 2d. Upon the fact that compounds of sodium and potassium impart peculiar colorations to non-luminous flames, like those of alcohol and of a mixture of coal-gas and air.

Prepare a mixture of a small teaspoonful of solutions (App., § 62) of almost any one of the salts of magnesium, sodium and potassium, and add to the mixture an equal bulk of chloride of ammonium. Pour a quarter of the mixture into a test-tube and the remainder into a small porcelain dish. Add to the contents of the test-tube two or three drops of a solution of phosphate of sodium, and as much ammonia-water, and shake the cold mixture at frequent intervals during one or two hours. A crystalline, white precipitate of phosphate of magnesium and ammonium will appear after a longer or shorter interval, according as the original solution was more or less dilute.

Test
for
Mg.

42. Evaporate the contents of the porcelain dish to dryness, ignite the residue until the chloride of ammonium has been completely expelled,— a point which will be indicated by the cessation of fuming,— allow the dish to cool, and pour into it three or four drops of water.

Carefully clean the loop on a piece of platinum wire by washing it repeatedly with water, and finally holding it in

the lamp flame until the last traces of sodium compounds are burned off, and it ceases to color the flame. With-
 Test for Na. out touching the loop with the fingers, dip it into the aqueous solution in the dish, and again hold it in the flame. A bright yellow color will be imparted to the flame by the sodium contained in the mixture; but the color peculiar to potassium compounds will be invisible, since the yellow color of the sodium overpowers and conceals it. Dip the loop a second time in the solution, and again hold it in the lamp flame; but this time look at the flame through a piece of deep-blue cobalt glass. This cobalt glass is the ordinary blue glass used for stained glass windows; it is essential that the glass should be of moderate thickness, and colored blue throughout, not simply "flashed" with blue. The character-

istic violet color imparted to a flame by potassium
 Test for K. compounds will now be visible, for the blue glass shuts off completely the yellow sodium light, while it permits the free passage of the violet rays.

Since traces of compounds of sodium and potassium are to be found almost everywhere, it is sometimes difficult to determine by the foregoing tests whether the substance under examination contains one or the other of these elements as an essential ingredient, or merely as an accidental impurity. It is always possible, however, to separate the sodium or the potassium from the other members of the class, and to decide, by actual inspection of the isolated compounds, whether one or both of these substances is contained in really appreciable quantity in the substance subjected to analysis. If only potassium is sought for, filter the aqueous solution, last mentioned, though a very small filter, add to the filtrate a drop or two of chlorhydric acid and several drops of a solution of bichloride of platinum (App., § 55). A yellow crystalline precipitate of chloroplatinate of potassium will separate after some time. Since chloride of ammonium would produce a similar precipitate, it is, of course, essential that the ammoniacal salt should be expelled by ignition before potassium is tested for.

In case sodium, or both sodium and potassium, be sought for, the magnesium must first be got rid of. To this end, moisten the dry residue, which contains the chlorides of magnesium, of potassium and of sodium, with a drop or two of water, mix it thoroughly with an equal bulk of red oxide of mercury and ignite the mixture until fuming ceases. The chloride of magnesium will be changed to oxide, while the easily volatile chloride of mercury escapes: —



The ignition should be effected beneath a chimney, or in a draught of air powerful enough to carry away the poisonous fumes of the corrosive sublimate. Boil the ignited residue with a small quantity of water; separate the insoluble oxide of magnesium, together with the excess of oxide of mercury, by filtration; evaporate the filtrate to a small bulk; throw down the potassium as chloroplatinate, collect the latter upon a filter, and from the filtrate remove the excess of chloride of platinum by means of sulphuretted hydrogen. Filter off the sulphide of platinum, and evaporate the filtrate to dryness to obtain the chloride of sodium. Or, instead of employing sulphuretted hydrogen, evaporate the filtrate from the chloroplatinate of potassium in a watch glass, at a gentle heat, until the liquid begins to become dry at its edges, and then examine it with a magnifying glass. Characteristic crystals of chloroplatinate of sodium will be seen in the form of long, slender prisms or needles of yellow color.

43. The Isolation of Class VII, by the removal of the preceding classes, has been described in § 12. Care must always be taken to concentrate the whole of the filtrate from Class VI by evaporation, before testing a portion of it for magnesium; and time enough must be allowed for the magnesium precipitate to crystallize. The remainder of the filtrate from Class VI must be evaporated to dryness and ignited, before testing for sodium and potassium, in order that the flame reactions of these elements may not be con-

TABLE FOR THE SEPARATION OF THE SEVEN CLASSES OF THE METALLIC ELEMENTS.

Add an excess of dilute HCl to the solution to be examined.		Saturate the filtrate with H ₂ S.	
A precipitate indicates	Boil the precipitate with NaHS.	Boil the filtrate, to expel H ₂ S, and add HNO ₃ , to oxidize Fe. Then add NH ₄ Cl and a slight excess of NH ₄ HO.	
	The alkaline filtrate is tested for	To the filtrate add a drop of NH ₄ HS.	
A residue indicates.	As Sb Sn [Au Pt]	A precipitate indicates	To the filtrate add a drop of (NH ₄) ₂ CO ₃ .
Pb Ag Hg (See § 17.)	Hg Pb Bi Cd Cu (See § 21.)	Fe Cr Al Ca ₃ P ₂ O ₈ etc.	A precipitate indicates
	(See § 25.)	Co Ni Mn Zn (See § 34.)	Evaporate the residual liquor to a small bulk, and test a portion of it for Mg (see § 41). Evaporate the rest of the solution to dryness; ignite and test for Na and K (see § 42).
	(See § 30.)	Ba Sr Ca (See § 38.)	

cealed or obscured by the vapors of ammonium salts, or by the combustion of particles of organic matter derived from the various reagents which have been added in the course of the analysis.

44. An outline of the methods employed for separating the several classes is presented in tabular form on the opposite page. The precautions necessary in the consecutive examination of an "unknown" solution for the members of the various classes have been already given under the several classes.

CHAPTER IX

GENERAL TESTS FOR THE NON-METALLIC ELEMENTS.

45. The following common elements remain to be considered: — Sulphur, nitrogen, phosphorus, carbon, boron, silicon, chlorine, bromine, iodine, fluorine, oxygen, hydrogen. It is obvious that oxygen and hydrogen cannot be directly sought for by any analytical process conducted in the wet way. These elements are added to the original matter in the water or acid which is used as a solvent. The presence of these elements is either inferred from the other results of the analysis, or forms the object of direct inquiry in the *preliminary treatment*, — that important part of every analysis which forms the main subject of Part II. The remaining elements all belong to that class vaguely described as *non-metallic*; they unite with oxygen, hydrogen, or both these elements, to form what are commonly called *acids*.

As the metallic elements are recognized through familiar compounds, hydrates, chlorides, sulphides, or other, so these non-metallic elements are identified by working out of the unknown mixture their characteristic compounds. These compounds are generally salts. But there is one marked difference between the search for the metallic and the search for the non-metallic elements in the wet way. In the case of iron and mercury it is commonly necessary to determine whether the element, if present, exists as a ferrous or ferric, as a mercurous or mercuric salt; but as a rule it is true that no question usually arises in connection with the determination of a metallic element, except the fundamental one of its presence or absence in a given solution. The sodium in the three

different salts, sulphate, sulphite and hyposulphite of sodium, for example, is detected by one and the same method; but, when the other elements of these salts are sought for, three different reactions will occur according to the varying nature of the ingredients other than sodium. A sulphate in solution gives one set of reactions, a sulphite another, and a hyposulphite a third. It is important to do more than determine the mere presence of sulphur and oxygen. We want to know whether the sodium salt be a sulphate, sulphite, or hyposulphite. Analogous questions arise with regard to other non-metallic elements; there is chlorine both in chlorides and chlorates, and carbon both in carbonates and oxalates. Arsenic, too, may be present in the form of arsenite or arseniate, and these two different kinds of salts exhibit many quite dissimilar reactions.

In the systematic analysis of an unknown substance, the examination for the metallic elements by the methods detailed in the previous chapter *invariably precedes* the determination of the non-metallic elements. Having ascertained which of the metallic elements are present in the substance under examination, the analyst tries to identify each class of salts which may be present by precipitating, or otherwise making manifest, some familiar member of that class. Thus he identifies sulphates by precipitating sulphate of barium, chlorides by precipitating chloride of silver, carbonates by throwing down carbonate of calcium, and so forth. The practically important inquiry is, how to find means of identifying each of the principal classes or kinds of salts. The word "class" or "kind" of salts is used in this connection as a collective name for all the salts which may be regarded as derived from one and the same acid; thus all sulphates constitute one class or kind, all carbonates another, and so forth. The following common classes of salts are those for which more or less perfect means of recognition will be given in this chapter:— Sulphates, sulphites, hyposulphites, sulphides, arseniates, arsenites, phosphates, carbonates, oxalates, tartrates, borates,

silicates, chromates, fluorides, chlorides, bromides, iodides, cyanides, nitrates, chlorates, acetates.

No system of successive testing and elimination, analogous to that already described for the metallic elements, has been devised for the non-metallic constituents of salts. There are, indeed, certain so-called *general reagents for acids*; but these reagents are chiefly useful to show the simultaneous presence or absence of members of *several* classes of salts, and hardly help towards the identification of any individual class, except in cases of the simplest sort, in which only a single class of salts is represented.

It sometimes happens that the preliminary examination (§ 80, 81) of the substance to be analyzed leads directly to some conclusion as to the class of salts in hand. A knowledge of the metallic element or elements present is moreover in most cases a great help in the determination of the other constituents. It is for this reason that the search for the metallic elements precedes the examination for the non-metallic. A single example will sufficiently illustrate, for the present, this important principle, which is of very wide application in qualitative analysis.

Suppose that the substance under examination is a solid which dissolves without difficulty in water and which proves to contain barium. From the presence of barium in a compound soluble in water, it is to be directly inferred that there is no sulphate, phosphate, carbonate, oxalate or tartrate in the original substance since these barium salts are *insoluble in water*. The list of salts excluded by the demonstrated presence of barium would be very long. So it is in greater or less degree with many other metallic elements. It is, indeed, no easy matter to make a solution containing even one representative of the seven classes into which the metallic elements have been divided, because each of these elements, except sodium and potassium, when present in a solution excludes one or more whole classes of salts. By attending to just inferences to be drawn from the quality of the metallic

elements, much time will be saved, and the want of a systematic procedure in searching for the non-metallic elements will be little felt. The presence of the arsenites and arseniates, of carbonates, chromates, cyanides, sulphides, sulphites and hyposulphites will ordinarily be revealed in the course of the search for the metallic elements.

Before giving the special tests by which the above-mentioned classes of salts are identified, we proceed to describe certain general tests which are of value, particularly when they give negative results.

46. The Barium Test. — When a solution of chloride (or nitrate) of barium is added in suitable quantity to a neutral or slightly alkaline solution containing representatives of any or all of the following classes of salts, precipitation usually occurs, for all these salts of barium are insoluble in water and alkaline liquids, if no ammonium salts be present: —

Sulphates,	Phosphates,	Silicates,
Sulphites,	Carbonates,	Chromates,
Hyposulphites,	Oxalates,	Fluorides.
Arseniates,	Tartrates,	
Arsenites,	Borates,	

If the chloride (or nitrate) of barium fail to produce a precipitate under the prescribed conditions, the complete absence of all the above thirteen classes of salts is at once demonstrated, provided that no ammonium salts be contained in the original solution.

47. Illustration of the Barium Test. — Prepare in a test-tube a solution containing at once sulphate, phosphate and carbonate of sodium; a very small bit of each salt will be sufficient. The solution will be found to be alkaline to litmus paper. Add to it chloride of barium (App., § 43), little by little, until a fresh addition of the reagent no longer produces an additional precipitate. The white precipitate consists of sulphate, phosphate and carbonate of

barium. All the thirteen barium salts which are liable to precipitation under these circumstances are white, with the single exception of chromate of barium. The yellow color of the chromate of barium (§ 38) distinguishes this one precipitate from all the rest. If this color is well marked, the presence of a chromate in the original solution (which must also have been yellow) may be inferred with certainty. In all other cases, however, the precipitate is white, as in the present experiment. The next question is, can anything further be learned from this white precipitate?

Add to the contents of the test-tube dilute chlorhydric acid, until the liquid has a decidedly acid reaction to litmus paper. An effervescence indicates the escape of carbonic acid, displaced by the less volatile chlorhydric acid. The bulky precipitate which the chloride of barium produced will in part disappear, but a portion of it remains undissolved. Filter the contents of the tube. The particles of precipitated sulphate of barium are so very fine that they often pass through the pores of the paper, necessitating repeated filtration through the same filter. To the filtrate add ammonia-water until the liquid has an alkaline reaction. A precipitate will reappear: the phosphate of barium which was dissolved by the chlorhydric acid is reprecipitated as soon as the acid solvent is neutralized by ammonia-water.

48. Of all the barium salts which might, in an actual analysis, be precipitated under conditions similar to those of the preceding experiment, only one, the sulphate of barium, is insoluble in chlorhydric and other strong acids. A separation of sulphur from a hyposulphite will not be mistaken for a barium precipitate (§ 19, p. 20). The fact that any of the original precipitate remains undissolved by the chlorhydric acid demonstrates the presence of a sulphate. The portion of the original precipitate which dissolved in the acid, and was reprecipitated by ammonia, consisted in this particular experiment of phosphate of barium; but in an actual analysis the possible salts represented would be so numerous as to make the indication of but little value.

If ammonia-water should cause no precipitation in the acid liquid which was filtered from the original precipitate, it must not be inferred that the acid of course dissolved nothing. The borate, oxalate, arseniate, arsenite, tartrate and fluoride of barium are all moderately soluble in solutions of ammoniacal salts, and may not be precipitated on the addition of ammonia. Of course, if the original solution contained ammonium salts, these six barium salts, if present in small quantity only, might fail to be precipitated. In fact, all the thirteen above-mentioned barium salts, except the sulphate, are more or less soluble in solutions of ammonium salts, so that, whenever ammonium salts are known to be present, there is really but one perfectly satisfactory indication with chloride of barium. The presence of a sulphate is revealed by it with certainty, but the results of the other tests must be received with some distrust.

If the original solution be acid, it is necessary to neutralize it with ammonia-water before the chloride of barium is added. Sometimes a precipitate is produced by the ammonia-water so added; in that case it is necessary to filter and proceed with the filtrate, although the ammonia-water may have thrown down salts of several of the classes above named, such as phosphates, oxalates and fluorides. (See also § 28, p. 37.) Even if the ammonia-water produce no precipitate, the testing is then performed under the disadvantage of the presence of ammonium salts.

If the original solution contained silver or lead salts, or mercurous salts, it would be impossible to use *chloride* of barium and chlorhydric acid as reagents; they would throw down the chlorides of those metals. Nitrate of barium (App., § 44) and dilute nitric acid must then be used.

The acids added to the precipitate formed by the barium salt must be always dilute acids. Chloride and nitrate of barium are themselves insoluble in concentrated chlorhydric and nitric acids, and if a strong acid were used as a solvent, the reagent salt might itself separate from the liquid.

49. The Calcium Test. — Chloride (or nitrate) of calcium precipitates the same classes of salts as chloride (or nitrate) of barium, with the single exception of the chromates. When *sulphates and all ammoniacal salts are absent*, or present only in minute quantities, something may be learned by testing a neutral or slightly alkaline solution supposed to contain representatives of some of the other classes of salts enumerated in § 46, with chloride or nitrate of calcium. The calcium salts liable to precipitation under these circumstances are all soluble in acetic acid, except the oxalate and the fluoride. The precipitate produced by the calcium reagent is, therefore, treated with acetic acid; if it completely redissolves, *oxalates and fluorides* are most probably *absent*. The presence of notable quantities of ammonium salts renders this test of uncertain value; because the fluoride and many other salts of calcium are soluble in solutions of ammonium salts. Since sulphate of calcium is sparingly soluble in water and acetic acid, the presence of a sulphate, causing precipitation of sulphate of calcium, obscures the reaction for oxalates and fluorides. Nitrate of calcium must be used instead of the chloride whenever silver or lead salts, or mercurous salts, are present in the solution under examination.

50. Illustration of the Calcium Test. — Prepare in a test-tube an aqueous solution of phosphate, oxalate and tartrate of sodium or potassium. A very small quantity of each salt will be enough. The solution will be neutral or faintly alkaline. Add to this solution a solution of chloride of calcium (App., § 42) until the precipitation is complete. Collect the white precipitate upon a filter, and, when drained, transfer it to a test-tube and treat it with acetic acid. The phosphate and tartrate of calcium will redissolve, but the oxalate remains untouched. To verify this result, and identify each one of the classes of salts present in the original solution, special tests, to be hereafter described, must be resorted to.

51. The Silver Test. — Nitrate of silver produces a precipitate in neutral or acid solutions with all chlorides, bromides, iodides and cyanides, and in neutral solutions with most of the classes of salts enumerated in § 46. In order to obtain the most comprehensive negative conclusion in the case that nitrate of silver produces no precipitate, it is necessary to operate upon a neutral solution. If, on the addition of nitrate of silver to a neutral solution, no precipitate appears after the lapse of several minutes, neither chlorides, bromides, iodides, cyanides nor sulphides can be present, and the absence of sulphites, hyposulphites, carbonates, phosphates, arseniates, arsenites, chromates, silicates, oxalates and tartrates may also be inferred with considerable certainty.

52. Illustration of the Silver Test. — Prepare in a test-tube a weak solution of chloride of sodium, iodide of potassium, cyanide of potassium and phosphate of sodium. Add nitrate of silver (App., § 39) to this slightly alkaline solution, until the precipitation is complete. The dense precipitate is yellowish-white. Pour dilute nitric acid into the mixture, until the solution is strongly acid; shake up the contents of the tube thoroughly, and after the lapse of several minutes collect the insoluble precipitate on a filter, and receive the filtered liquid in a test-tube.

Neutralize the filtrate with ammonia-water: a yellow precipitate of phosphate of silver will reappear.

Wash the precipitate on the filter thoroughly to free it from the superfluous nitrate of silver. Rinse the washed precipitate into a clean test-tube, decant the water from above it, pour over it ammonia-water, and gently heat the mixture. The silver precipitate will visibly diminish in bulk, but a yellowish portion remains undissolved. Filter again, and neutralize the filtrate with nitric acid; a white precipitate will fall.

This experiment proves that a portion, but not all, of the mixed silver salts which are insoluble in nitric acid, are solu

ble in ammonia-water. The *chloride*, *cyanide* and *bromide* of silver dissolve in ammonia-water, the latter with difficulty; the *iodide* remains undissolved. Special tests, hereafter to be described, are applied in order to confirm the presence of iodine, and to detect each and all of the three substances which are liable to be confounded in the white precipitate just mentioned.

53. In the application of the silver test to the examination of a substance of unknown composition, it is, of course, most advantageous to work with a neutral solution, as in such a case the absence of any precipitate would lead to the inference that all the salts mentioned in § 51 are absent: if the solution is neutral, the nitrate of silver may be added directly to a portion of it. In addition to the classes of salts mentioned in § 51, if the original solution contained any considerable quantity of a borate, the borate of silver would be precipitated under these conditions; but a small proportion of some borate might escape precipitation. If the original solution be acid to test paper, add nitrate of silver to a portion of it in a test-tube, and then pour in upon the liquid some dilute ammonia-water, so gently that the two liquids do not mix at once. At some layer near the junction of the two dissimilar liquids, the fluid must be neutral. If at that layer no precipitate or cloud appear, the twelve kinds of salts above enumerated are absent. If the original solution is alkaline, dilute nitric acid is to be added in precisely the same manner as the ammonia-water in the opposite case. The neutral layer between the two liquids is attentively observed, and the absence of any film or cloud therein justifies the same sweeping conclusion as that above given.

Some conclusions may often be drawn from the color of the precipitate produced by nitrate of silver. Chloride, bromide, cyanide, oxalate, tartrate, and borate of silver are white; iodide, phosphate, and arsenite of silver are yellow; silicate of silver is yellow or white; arseniate of silver is brownish-red; chromate of silver is purplish-red; sulphide

of silver is black. When the silver precipitate is white, black, or of some obscure, indecisive color, the operations in the wet way at this stage should be directed to proving or disproving the presence of chlorides, bromides, iodides, cyanides and sulphides. To this end the portion of the original solution which has been already tested with nitrate of silver, should be made decidedly acid with dilute nitric acid. Of all the silver salts which can be precipitated on the addition of nitrate of silver, only the chloride, bromide, iodide, cyanide and sulphide can resist dilute nitric acid. If the precipitate once formed redissolves completely in nitric acid, no chloride, bromide, iodide, cyanide or sulphide was present in the original solution. If, on the contrary, a residue remain, one or more of these kinds of salts must have been represented in the original solution. If the residue be black or blackish, the presence of a sulphide is to be inferred; if it be white or whitish, the absence of sulphides and the presence of a chloride, bromide or cyanide is to be inferred; if it be distinctly yellowish, an iodide is probably present. When the liquid under examination contains a ferrous salt, protochloride of tin, or any other active reducing agent, metallic silver is liable to be precipitated as a dark, heavy powder. The examination for the metallic element will generally have revealed the presence of any such agent.

It is to be remarked that cyanide of mercury does not give a precipitate with nitrate of silver. When mercury has been detected in the substance under examination, cyanogen must be sought for in other ways (§ 58) than this.

54. Nitrates, Chlorates and Acetates. — It is quite clear that no method of precipitation whatever will apply to nitrates, chlorates and acetates, since these kinds of salts are all soluble. No insoluble nitrate, chlorate, or acetate is known. Special tests must be sought for these three classes of salts.

CHAPTER X.

SPECIAL TESTS FOR THE NON-METALLIC ELEMENTS.

55. We now proceed to indicate the most available special tests for the non-metallic elements and their commonest compounds. It is noteworthy that the non-metallic elements enter into composition under various forms, which produce, with one and the same metallic element, various salts. Thus within the narrow range of this treatise, sulphur is to be sought in sulphides, sulphates, sulphites and hyposulphites; carbon in cyanides, acetates, carbonates, oxalates and tartrates, and arsenic in arsenites and arseniates. The various classes of salts will be taken up successively. It should be premised that these special tests are sometimes applied to the original solution *before* the precipitation with chloride of barium and nitrate of silver, and sometimes *during or after* these more general testings. In the first case, the student is seeking guidance in the application of the more comprehensive tests; in the latter case, he is trying to confirm results already almost sure.

56. Effervescence. — When a solution containing a carbonate, cyanide, sulphide, sulphite, or hyposulphite, or a mixture of representatives of some or all of these kinds of salts, is treated with chlorhydric acid and then warmed, an evolution of gas occurs with more or less effervescence. The gases evolved are all colorless; but they all have very characteristic odors except carbonic acid, the gas which escapes from a carbonate. A cyanide gives off the pungent odor of cyanhydric acid. A sulphide yields sulphuretted hydrogen of familiar presence. Sulphurous acid escapes from sulphites

and hyposulphites alike; but in the latter case a deposition of sulphur makes the liquor turbid. If only one of these gases were present, the effervescence and the odor, or the absence of odor, would identify it; but when mixtures are to be dealt with, further means of identification are necessary.

57. Carbonates.— To prove the presence of carbonic acid gas, when effervescence has occurred, add chlorhydric acid, little by little, to the effervescing solution, until the acid is decidedly in excess; meanwhile keep the mouth of the test-tube loosely closed with the thumb to promote the accumulation of the gas evolved. When the tube is supposed to be full, carefully decant the gas into a second test-tube containing a teaspoonful of lime-water (App., § 41), taking care not to allow any of the liquid to pass over with the gas. Mix the lime-water and the gas in the second test-tube by thorough shaking. A white precipitate of carbonate of calcium will be produced, if the gas tested is, or contains, carbonic acid.

If the effervescence is slight, and the quantity of gas evolved seems too small to be decanted in this way, dip the end of a dark-colored glass rod into lime-water, and thrust the moistened end into the test-tube, bringing it close to the surface of the fluid. If the gas be carbonic acid, the lime-water adhering to the rod will become visibly turbid.

The student who desires to see the working of this test before having occasion to apply it in an actual analysis, can operate upon a morsel of carbonate of sodium dissolved in a little water.

58. Cyanides.— When the smell of the gas which escapes from the solution under examination (§ 56), or the qualities of the precipitate with nitrate of silver (§ 53), give occasion to suspect the presence of a cyanide, the following confirmatory test may be resorted to:— Add to the solution supposed to contain free cyanhydric acid; or an alkaline cyanide, a few drops of a solution containing both a ferrous and a ferric salt (a solution of ferrous sulphate which has

been exposed to the air, for example), and a small quantity of caustic soda solution. If cyanogen is present, a bluish-green precipitate forms, which consists of a mixture of Prussian blue and the hydrates of iron. Warm the liquid, and add to it an excess of chlorhydric acid. The hydrates of iron dissolve, but the Prussian blue remains undissolved.

In case the proportion of cyanogen is small, the precipitated hydrates of iron may conceal the Prussian blue until the addition of the acid; and in the case of minute quantities the liquid simply appears green after the addition of chlorhydric acid, and it is only after long standing that a trifling blue precipitate separates from it.

This test may be well illustrated by means of a small particle of cyanide of potassium dissolved in a teaspoonful of water.

To detect cyanogen in cyanide of mercury, it is necessary to precipitate the mercury as sulphide, by means of sulphuretted hydrogen, and to identify the free cyanhydric acid in the filtered or decanted fluid.

59. Sulphides. — Many sulphides give off sulphuretted hydrogen when heated with chlorhydric acid. If the quantity of gas is so small that its odor is imperceptible, the lead paper test (§ 32) should be applied.

When sulphides are dissolved in nitric acid or aqua regia, their sulphur is partly separated in a free state and partly converted into sulphuric acid. The free sulphur is identified by its color and texture, and by its behavior when burnt. The sulphuric acid in the liquid is detected in the usual manner (§ 64).

60. Sulphites. — All the sulphites evolve sulphurous acid, without any deposition of sulphur, when treated with chlorhydric acid. The very sharp odor of this gas is enough to identify it.

As has been before stated, nitrate of silver produces in solutions of sulphites a white precipitate; but this precipitate blackens when the liquid is boiled, on account of the reduction of silver.

When the sulphites are heated with strong nitric acid, or other powerful oxidizing agent, they are converted into sulphates without precipitation of sulphur. The sulphates so produced may be identified in the usual way (§ 61).

61. Hyposulphites. — The hyposulphites disengage sulphurous acid and deposit sulphur when warmed with chlorhydric acid. This decomposition is not immediate if the solution be dilute.

The precipitate produced in the solution of a hyposulphite by nitrate of silver, dissolves again readily in an excess of the hyposulphite. On standing, the precipitate of hyposulphite of silver turns black spontaneously, being decomposed into sulphide of silver and sulphuric acid. Heating produces this effect almost immediately.

Hyposulphite of sodium is a good salt from which to get the above reactions of hyposulphites.

62. Chromates. — Chromium is detected during the examination for the metallic elements, and the analyst generally obtains pretty certain evidence concerning the actual condition in which this element enters into the substance under examination, whether as chromate or salt of chromium; for the chromates are reduced by sulphuretted hydrogen with change of color and deposition of sulphur as stated in § 23.

To confirm the indications thus obtained, the following tests are used: — When acetate of lead (App., § 45) is added to a neutral solution of a chromate, yellow chromate of lead separates, insoluble in acetic acid, but soluble in caustic soda.

As has been before stated, the purplish-red color of chromate of silver (§ 53), and the yellow color of chromate of barium (§ 48), are valuable indications of the presence of a chromate.

A solution of normal chromate of potassium is the best substance from which to obtain for the first time the reactions of the chromates.

63. Arsenites and Arseniates. — The presence or absence of arsenic is determined in the search for the metallic elements by the tests already given in the treatment of Class III. These tests, however, do not indicate which class of compounds (arsenic or arsenious) is present in the solution under examination. In whatever form present, the arsenic would be precipitated as the *tersulphide* (As_2S_3), and subsequently converted into an *arsenate* by fusion with nitrate of sodium. Discriminating tests must therefore be applied to the original solution.

The tests by which an arseniate may be identified have already been given (§§ 25, p. 31). It may be remarked further that the presence of this class of arsenic compounds is often inferred by the length of time required to saturate with sulphuretted hydrogen a solution containing arsenic acid or an arseniate. The arsenic acid is first reduced to arsenious acid and then precipitated; a separation of sulphur accompanies the reduction.

A solution of an arsenite yields with nitrate of silver a yellow precipitate of arsenite of silver under the same conditions in which an arseniate gives the brownish-red precipitate. The silver test generally serves to distinguish between arsenites and arseniates, but circumstances may arise in which it would be inapplicable. The following test affords further means of discrimination: —

If to a solution of arsenious acid or an arsenite, caustic soda be first added in excess, and then five or six drops of a dilute solution of sulphate of copper, a clear bluish liquid is obtained, which, upon boiling, deposits a red precipitate of suboxide of copper (Cu_2O), while soluble arseniate of sodium is simultaneously produced, and remains in the solution. This test is good as a means of distinguishing between arsenites and arseniates when no organic matters are contained in the solution under examination. The qualification is necessary, because grape-sugar and many other organic substances exercise a like reducing action on copper salts.

64. Sulphates. — The barium test (§§ 46–48) is all sufficient for the detection of sulphates. The operator should make sure that the chlorhydric acid itself contains no sulphuric acid, that an excess of acid is really present, and that the solution is tolerably dilute. Concentrated acids and strong solutions of many salts impair the delicacy of the reaction.

65. Phosphates. — When the previous steps of the analysis have proved that the phosphates present in the solution under examination are soluble in ammoniacal liquids, and that no arsenic acid or arseniates are present, the following test will identify a phosphate or free phosphoric acid.

Add to the solution to be tested a clear mixture of sulphate of magnesium, chloride of ammonium and ammonia-water. When a phosphate or free phosphoric acid is present, a white, crystalline precipitate of phosphate of magnesium and ammonium is formed, even in very dilute solutions. Stirring and shaking promote its separation. The precipitate dissolves readily in acids.

When arsenic acid or arseniates are present in the original mixture, this test for phosphates can still be applied, if all the arsenic be previously removed by precipitation as sulphide (§ 24). The magnesium mixture can be used in the filtrate from the sulphide of arsenic, after it has been boiled to expel the sulphuretted hydrogen.

The preceding test can only be applied when the phosphate present is soluble in ammoniacal solutions. The following test is of much more general application; it can be used in presence of arsenic acid, and is applicable to either neutral or acid solutions of phosphates; it is also extremely delicate.

When two or three drops of a neutral or acid solution of a phosphate (even of iron, aluminum, barium, strontium, calcium or magnesium [compare § 28]) are poured into a test-tube containing four or five teaspoonfuls of a solution of molybdate of ammonium in nitric acid (App., § 21), there is

formed *in the cold* a pale-yellow precipitate which is apt to gather upon the sides and bottom of the tube. If the precipitate does not appear in a few minutes, a few drops more of the solution to be tested may be added. This precipitate is soluble in an excess of phosphoric and other acids; and certain organic substances also prevent its formation. A yellow coloration of the liquid merely is not enough to prove beyond question the presence of a phosphate; a precipitate must be waited for. The yellow precipitate can be easily recognized, even in dark-colored liquids, when it has settled. The solution to be tested must not be heated, nor must it be more than blood-warm.

Phosphate of sodium is the best substance on which to try the test for phosphates.

66. Oxalates. — The precipitation of white, finely-divided oxalate of calcium, by all soluble calcium salts from solutions of oxalates or oxalic acid, has been already described (§ 50). Even the solution of sulphate of calcium gives this reaction with oxalates.

If oxalic acid, or an oxalate in the dry state, be heated in a test-tube with an excess of concentrated sulphuric acid, a mixture of carbonic oxide and carbonic acid is set free with effervescence; the carbonic acid may be identified by the lime-water test; and if the quantity operated upon is considerable, the carbonic oxide may be inflamed at the mouth of the tube.

67. Tartrates. — Tartaric acid and the tartrates, when heated in the dry state, char, and emit a very characteristic odor which somewhat resembles that of burnt sugar. Strong sulphuric acid blackens tartaric acid and the tartrates. This is the only class of salts among all those within the scope of this treatise, which exhibit this carbonization by sulphuric acid.

To confirm the presence of tartaric acid, or a tartrate, in any liquid supposed to contain it, a concentrated solution of acetate of potassium is added to the liquid, and the mixture

violently shaken. The precipitate, when one forms, is a difficultly soluble acid tartrate of potassium. The addition of an equal volume of alcohol increases the delicacy of the reaction. The more concentrated the solution to be tested the better. To prepare the required solution of acetate of potassium at the moment of use, rub together in a dish half a teaspoonful of carbonate of potassium and as many drops of acetic acid as will dissolve three quarters of the carbonate; throw the mixture on a small moistened filter and use the filtrate.

Tartaric acid is a good substance from which to get these reactions.

68. Borates.—To confirm the presence of a borate, strong sulphuric acid is mixed with the dry substance under examination in quantity sufficient to make a thin paste, and an equal bulk of alcohol is added to the mixture. The alcohol is then kindled. Boracic acid imparts to the alcohol flame a yellowish-green color. The test is made more delicate by stirring the mixture, and by repeatedly extinguishing and rekindling the flame. Copper salts impart a somewhat similar color to the flame; but this metal, if present, may be got rid of by sulphuretted hydrogen before testing for boracic acid.

If a solution of boracic acid, or of a colorless borate, is mixed with chlorhydric acid to slight, but distinct, acid reaction, and a slip of turmeric paper is dipped half way into the liquid and then dried at 100° C., the dipped half shows a peculiar red tint. This test is delicate, but there are a few other solutions which impart, not the same, but somewhat similar tints to turmeric paper. The yellow turmeric paper used for this test is prepared by steeping narrow strips of white paper in a filtered tincture of turmeric root. The dried paper should have a fine yellow color. The tincture is made by digesting one part of bruised turmeric in six parts of warm spirits of wine.

The reactions of borates may be obtained with a fragment of borax.

69. Silicates.—The silicates of sodium and potassium are the only silicates which are soluble in water. The solutions of these alkaline silicates are decomposed by all acids. If chlorhydric acid is added gradually to a strong solution of an alkaline silicate, the greater part of the silicic acid separates as a gelatinous hydrate. As a rule, the more dilute the fluid, the more silicic acid remains in solution.

If the solution of an alkaline silicate, mixed with chlorhydric or nitric acid in excess, be evaporated to dryness, silicic acid separates; if the dry mass be ignited and then treated with dilute chlorhydric or nitric acid, the whole of the silicic acid remains insoluble in the free state, as a gritty, whitish powder, while the other substances dissolve.

A solution of chloride of ammonium produces a gelatinous precipitate in strong and moderately dilute solutions of the alkaline silicates. This precipitate is hydrated silicic acid containing alkali.

A solution of waterglass is the best substance in which to study the reactions of the silicates of the alkali-metals.

70. Fluorides.—If a finely-pulverized fluoride is heated with concentrated sulphuric acid in a small leaden capsule or platinum crucible, fluorhydric acid is disengaged.

Coat with wax the convex face of a watch-glass large enough to cover the capsule, by heating the glass cautiously, and spreading a small bit of wax evenly over it while the glass is hot. Trace some lines or letters through the wax with a pointed instrument of wood or horn. Fill the hollow of the glass with cold water, and cover with it the capsule which contains the fluoride mixture. Heat the capsule *gently* for half an hour or an hour. Then remove the watch-glass, dry it, heat it cautiously to melt the wax, and wipe it with a bit of paper. The lines or letters traced through the wax will be found etched into the glass. A barely perceptible etching is made more visible by breathing upon the glass. If much silicic acid is present, this reaction fails.

When a fluoride, naturally combined or artificially mixed

with silica, is heated with strong sulphuric acid, fluoride of silicon is evolved. This reaction is available as a test for fluorine.

A mixture of the supposed fluoride and fine dry sand is heated in a short, dry test-tube with concentrated sulphuric acid. A drop of water, caught in the loop of a clean platinum wire, is held in the mouth of the test-tube. This drop of water becomes merely dim, quite opaque, or almost solid with silicic acid, according to the quantity of fluoride of silicon evolved from the mixture. The gaseous fluoride of silicon shows white fumes when it comes in contact with moist air. If a considerable quantity of fluoride of silicon be evolved from the mixture tested, it can be decanted into another test-tube, and there shaken up with water. If the substance to be tested for fluorine is known to contain silica, it is, of course, unnecessary to add sand to it. This method applies to all fluorides decomposable by hot sulphuric acid. It is evident that this test reversed can be applied to the detection of silica.

Fluoride of calcium (fluor-spar) is a good material from which to obtain these two tests for fluorine.

71. Chlorides. — The following confirmatory test is applied to chlorides in the dry state.

When a chloride, in powder, is heated in a test-tube with black oxide of manganese and strong sulphuric acid, chlorine gas is evolved; this gas is recognized by its odor, greenish-yellow color, and reaction with iodo-starch paper. The gas evolved by a chloride gives no colored reaction with starch alone; but when a moistened slip of paper, on which a mixture of starch paste and iodide of potassium (App., § 38) has been spread, is held in an atmosphere or current of chlorine, the paper is colored blue in consequence of the liberation of iodine which the chlorine effects. The yellow color of the gas is best seen by looking lengthwise through the tube.

It is often difficult to obtain black oxide of manganese which will not of itself give a reaction for chlorine when

treated with pure sulphuric acid. Instead of this reagent, *pure* bichromate of potassium in powder may be employed. The sulphuric acid used should be diluted with an equal bulk of water. The action which takes place is similar, except that the chlorine is accompanied by chlorochromic acid (CrClO_2) which in part condenses as a yellow liquid on the sides of the tube. The reaction on iodo-starch paper is, however, obtained without difficulty.

Mercurous chloride (calomel) gives no reaction for chlorine when treated with binoxide of manganese (or bichromate of potassium) and sulphuric acid. The chlorine may be detected, however, by treating the salt in powder with zinc and dilute sulphuric acid. The mercury is reduced to the metallic state and the chlorine goes into solution as chloride of zinc; in this solution the chlorine may be discovered by the ordinary tests.

72. Bromides. — The confirmatory tests for bromides depend upon the setting free of bromine itself.

Hot nitric acid liberates the bromine from all bromides except those of silver and mercury. In solutions, the free bromine produces a yellow coloration; when set free from solid bromides in a long and narrow tube, the brownish-yellow vapors of bromine condense into a liquid upon the cold walls of the tube.

When bromides, in powder, are heated in a test-tube with black oxide of manganese (or bichromate of potassium) and strong sulphuric acid, brownish-red vapors of bromine are evolved. If chlorides are also present, the bromine will be mixed with chlorine.

To identify bromine and distinguish it from chlorine, moistened starch is brought into contact with the free bromine. A yellow or orange-yellow coloration of the starch marks the presence of bromine. To apply this test, thrust a rod smeared with starch-paste into the tube which contains the bromine vapors; or, when greater delicacy is requisite, perform the experiment which is expected to liberate bromine in a very

small beaker, and cover this beaker with a watch-glass to whose under side is attached a bit of paper moistened with starch-paste and sprinkled with dry starch.

Bromide of potassium is a good substance with which to study the tests for bromine.

73. Iodides. — When an iodide, in the solid form or in solution, is heated with strong nitric acid, iodine is liberated and sublimes in violet vapors.

Free iodine in vapor is recognized by the deep blue color which it imparts to starch-paste. Vapors may be tested by bringing into contact with them a glass rod smeared with thin starch-paste, or a slip of white paper on which the paste has been spread.

The best method of detecting iodine in a solution is to add a few drops of thin, clear starch-paste to the liquid, and then set free the iodine by means of nitrite of potassium (App., § 37), as follows: — The cold fluid to be tested is acidulated with dilute chlorhydric or sulphuric acid, after the addition of the starch-paste, and a drop or two of a concentrated solution of nitrite of potassium is then added. A dark blue color will be instantly produced. It is essential that the liquid should be kept cool, for the blue coloration is destroyed by heat.

Like chlorine and bromine, iodine is liberated by heating an iodide with black oxide of manganese (or with bichromate of potassium) and sulphuric acid. The iodine so liberated is readily distinguished by the above tests.

The student can try all these tests for iodine with a small crystal of iodide of potassium.

74. Nitrates. — The preliminary examination generally gives warning of the presence of a nitrate: to confirm the presence of a nitrate, one or both of the two following tests may be used: —

If the solution of a nitrate is mixed with an equal volume of strong sulphuric acid, the mixture cooled in cold water, and a concentrated solution of ferrous sulphate then cautiously

added to it in such a way that the two fluids do not mix, the stratum of contact shows a purple or reddish color, which changes to a brown. If the fluids are then mixed, a clear brownish-purple liquid is obtained. The color fades on heating. Another way of performing the same test is to drop a crystal of copperas into the cold mixture of nitrate and sulphuric acid. There forms around the crystal a dark halo, which disappears with a kind of effervescence on the application of heat. It is, of course, essential that the sulphuric acid employed for this test should be so free from nitric and hyponitric acids, as not itself to give this reaction with ferrous sulphate.

Boil some chlorhydric acid in a test-tube, add to it one or two drops of a dilute solution of sulphindigotic acid (App., § 57), and continue the boiling a moment. If the chlorhydric acid is sufficiently free from chlorine, the resulting liquid will be of a faint blue color. If a nitrate, either solid or in solution, be added to this liquid and the mixture be again boiled, the liquid will be decolorized. This reaction is delicate; but there are some other substances, especially free chlorine, which have a like bleaching effect.

Nitrate of potassium is a suitable material on which to illustrate the tests for nitrates.

75. Chlorates. — The preliminary examination gives warning of the presence of chlorates.

When a few particles of a chlorate in the solid form are covered with two or three times as much strong sulphuric acid, and the mixture is *gently* warmed, the liquid becomes intensely yellow, and a greenish-yellow irritating gas of peculiar odor (hypochloric acid, ClO_2) is evolved, which explodes with violence at a moderate heat. After this decomposition, the gas evolved has the characteristic odor of chlorine. The quantity of chlorate operated upon should be very small.

The solution of a chlorate decolorizes indigo-solution precisely like the solution of a nitrate, under like conditions (§ 74).

A chlorate is converted by ignition into a chloride, from a solution of which nitrate of silver precipitates the chlorine.

Chlorate of potassium illustrates very well the reactions of chlorates.

76. Acetates.—When acetates are moderately heated with strong sulphuric acid, hydrated acetic acid distils from the mixture, and may be recognized by its pungent odor.

When an acetate is heated with alcohol and sulphuric acid in equal volumes, acetic ether is formed. The agreeable odor of this ether is highly characteristic.

Hot concentrated sulphuric acid produces no blackening with an acetate.

When a few drops of a solution of ferric chloride (App., § 48), are added to a solution of a neutral acetate, or to a solution of an acetate previously neutralized with ammonia, the liquid acquires a dark red color, because of the formation of ferric acetate. If the liquid contain an excess of the acetate, a basic acetate of iron is precipitated in yellow flocks upon boiling, and the fluid finally becomes colorless.

Acetate of sodium may be used to show these reactions of the acetates.

76a. Oxides and Hydrates.—In case the substance under examination is an oxide or a hydrate, it may in general be recognized by the known properties of the oxide or hydrate of the metallic element which has been found to be present. The hydrates (except of the alkalies) give off water when heated, and many oxides and hydrates when heated with charcoal in a closed tube give off carbonic acid or carbonic oxide. Peroxides may generally be distinguished by their giving off oxygen when heated, or by causing an evolution of chlorine when treated with chlorhydric acid.



PART SECOND.

THE ACTUAL EXAMINATION OF SUBSTANCES OF UNKNOWN COMPOSITION.

77. The substance to be examined may be either solid or liquid. We shall consider first the treatment of a solid; afterwards that of a liquid. The solid may be a metallic substance, that is, a pure metal or an alloy, or it may be a salt, mineral, or other non-metallic body. The method of procedure differs in the two cases. We shall describe first the treatment of a salt, mineral, or other non-metallic substance. The two following observations, however, apply to all cases. The student should, in the first place, learn as much as possible from the external properties of the substance to be analyzed, from its color, consistency and odor, if it is a liquid; from its color, texture, odor, lustre, hardness, gravity and crystalline or amorphous structure, if it is a solid. By attentively observing the characteristics or individual peculiarities of every substance which passes through his hands, the student will soon learn to recognize many substances at sight, — by far the quickest and easiest way of identifying them. Secondly, since the original substance must be several times reverted to in order to complete an analysis, the student should husband his stock of the substance to be analyzed, never employing the whole of it for any single course of experiment. It is well also to reserve a portion for unforeseen contingencies.

CHAPTER XI.

TREATMENT OF A SALT, MINERAL, OR OTHER NON METALLIC SOLID.

ORDER OF PROCEDURE.

78. THE general course pursued in the analysis of a non-metallic solid substance consists, as a rule, in: — 1st. The *preliminary examination*, to be presently described; 2d. The bringing the substance into solution; 3d. The examination of the solution obtained for the metallic elements according to the methods laid down in Part I, Chaps I-VIII; 4th. The application of such general and special tests for the non-metallic elements as may not have been rendered unnecessary by facts observed during the preceding course of the analysis.

A. PRELIMINARY EXAMINATION IN THE DRY WAY.

79. The preliminary examination in the dry way consists essentially of two operations; the substance is first subjected to the influence of heat alone (*closed-tube test*, § 80); and afterwards a second portion of the substance, or, in some cases, the same portion, is exposed to the influence of heat and certain reducing agents (*reduction test*, § 81).

80. Closed-Tube Test. — Prepare a hard glass tube No. 4 (App., § 2), about three inches long, and closed at one end. Let fall into this tube a minute fragment of the solid, or a little of its powder. If the substance be used in powder, wipe out the tube with a tuft of cotton on a wire, in order that the interior walls of the tube may be clean to receive a sublimate. Heat the substance at the end of the tube, at first gently in the lamp, but finally intensely at the

highest temperature to be obtained with the Bunsen gas-lamp, or in the blowpipe flame. The following are the most noteworthy reactions with the inferences to be drawn from them; it not unfrequently happens that a single substance gives several of these reactions.

I. *The substance blackens*, and gases or vapors are evolved. These vapors often have a disagreeable smell, sometimes like that of burnt sugar, paper, or feathers. Sometimes they condense in tarry droplets; water also condenses on the cold part of the tube. These appearances indicate the presence of organic substances.

Now the presence of fixed organic matter interferes with the detection of many substances, and it must be destroyed before the analysis can be proceeded with. The method employed to this end is detailed on page 97; no matter whether the substance contain organic matter or not, the closed-tube test is immediately succeeded by the reduction test.

Simple blackening is not proof of the presence of organic bodies. Some salts of copper and cobalt, for example, blacken through the formation of a black oxide.

When organic matter is shown to be present, the student should look particularly, at the proper stage of the analysis, for acetates (§ 67) and tartrates (§ 67); but he will not forget that there are hundreds of organic compounds which are not comprehended in the plan of this treatise.

II. *The substance is not carbonized*, but vapors or gases escape from it. The most important are: —

a. *Aqueous vapor*, which condenses in the upper part of the tube. Test this water with litmus paper; if it is alkaline, ammonia may be suspected; if acid, some volatile acid (H_2SO_4 , HCl , HBr , HI , HF , HNO_3 , etc).

b. *Oxygen* recognized by its relighting a glowing match. This gas indicates nitrates, chlorates and peroxides. If the heated substance fuses, and a small fragment of charcoal thrown in is energetically consumed, the presence of a nitrate or chlorate may be assumed.

c. *Hyponitric acid*, recognized by the brownish-red color of the fumes. It results from the decomposition of nitrates.

d. *Sulphurous acid*, recognized by its odor. It not unfrequently results from the decomposition of sulphates, sulphites and sulphides.

e. *Carbonic acid*, derived from decomposable carbonates, and to be recognized by lime-water (§ 57).

f. *Cyanogen*, derived from decomposable cyanides, and to be recognized by its odor, and by the blue flame with which it burns when there is enough of it to be lighted.

g. *Sulphuretted hydrogen*, derived from moist sulphides, and to be known by its smell.

h. *Ammonia*, resulting sometimes from the decomposition of ammoniacal salts.

III. *A sublimate forms* beyond the heated portion of the tube. The whole of the substance may volatilize. The following are the commonest sublimates:—

a. *Sulphur*, which sublimes in reddish drops. The sublimate becomes solid and yellow, or yellowish-brown, on cooling.

b. *Ammonium salts* give white sublimates.

Test a separate small portion of the original substance for the salts of ammonium, by mixing it in a small test-tube with an equal bulk of slaked lime and a few drops of water, and heating the mixture. Ammonia, when evolved, may be recognized by its smell, and by the white fume produced when a rod moistened with a mixture of equal parts of strong chlorhydric acid and water is held above the mouth of the tube. Unless the original solid is obviously inalterable by heat, it should be *invariably* tested in this way for ammonium salts.

c. *Metallic mercury and some of its compounds*. The metal sublimes in metallic droplets. The two chlorides of mercury give sublimates which are white when cold. The red iodide of mercury gives a yellow sublimate. The sulphide of mercury gives a dull black sublimate.

d. *Arsenic and some of its compounds.* Metallic arsenic gives a black sublimate of metallic lustre. Arsenious acid gives a white sublimate which looks crystalline under a magnifying lens. The sulphides of arsenic give sublimates which are brownish-red while hot, but reddish-yellow to red when cold; these sublimates look not unlike that of pure sulphur.

e. *Teroxide of antimony* first fuses to a yellow liquid and then gives a white sublimate, composed of needle-like crystals.

f. *Oxalic acid* gives a white, crystalline sublimate with dense fumes in the tube.

Other reactions besides those just mentioned sometimes occur during the examination of a substance in the closed-tube: they are, however, of less importance and, in fact, the inferences to be drawn from the appearances already indicated are of very unequal value. Thus the detection of organic matter is of the first importance, because, as has been stated, such matters must be got rid of before the analysis can be proceeded with. Again the presence, or entire absence, of ammonium salts should be put beyond doubt at this first stage of the examination. Thirdly, the presence of mercury, or of mercurous salts, determines the choice of the acid solvent in favor of nitric acid, in case water will not dissolve the substance under examination (§ 85), and the presence of mercuric salts renders necessary the substitution of sulphhydrate of ammonium for sulphhydrate of sodium as the solvent for the sulphides of Class III (§ 27). Accordingly, it is useful to get information of the presence of mercury or its compounds at this early stage of the examination. As to the other appearances, they give information which may be convenient, but is never essential for the safe conduct of the regular course of analysis. Practically the closed-tube test may generally be conducted as follows:—

The substance is introduced into the tube as stated above, a strip of moistened litmus paper is folded loosely across the mouth of the tube, and the tube heated in the lamp, at first very gently. The deportment of the substance is observed

under the gentle heat at first applied and also as the heat increases, the appearance of condensed moisture or of other sublimate is looked for, and any action of escaping vapors on the litmus paper is noted. Meanwhile the tube is occasionally removed from the lamp, to see whether any peculiar odor of escaping gas may be detected. Finally any water which may have condensed in the tube is tested with litmus paper. The student should note any other appearances, whether mentioned above or not, which manifest themselves during the examination, as they may serve as corroborative tests when the composition of the substance has finally been made out with some certainty.

81. Reduction Test.—Mix a little of the powder of the substance under examination (the bulk of a hemp-seed) with an equal quantity of carbonate of sodium, and make the mixture into a pasty ball with a small drop of water. Select a piece of dry, well burned, soft-wood charcoal, and cut out of it a rectangular block about 6 inches long, $1\frac{1}{2}$ in. wide, and $\frac{1}{2}$ to $\frac{3}{4}$ in. thick, having its flat, smooth surface (6 in. by $1\frac{1}{2}$ in.) at right angles to the rings of growth in the tree. It is this surface which is always to be used. A good piece of charcoal may be made to serve for many assays by filing off the used surface and exposing a new one, but ordinary charcoal allows portions of the flux or even small metallic globules to run into its pores or into cracks opened by the heat, and can rarely be used with advantage the second time. At a quarter to half an inch from the end of the piece of charcoal, scoop out with a penknife a little cavity of the size of half a pea. Place the prepared pellet in this cavity, and expose it for several consecutive minutes to the reducing flame of the blowpipe (App., § 78).

Under these conditions, vapors of characteristic odor or appearance may be evolved; some of them will be mentioned below. The two objects, however, to which attention is specially to be directed, are the residue in the cavity, and the incrustation on the charcoal outside of the cavity.

The following metals may be found as fused metallic globules in the cavity; lead, silver and gold are reduced with ease, even by an inexperienced operator; tin and copper with some difficulty: —

- a. Gold — a yellow, malleable globule, produced without incrustation.
- b. Copper — a red, malleable globule, produced without incrustation.
- c. Tin — a bright, white, malleable globule. An incrustation is simultaneously produced, which is faint yellow when hot and white when cold; it immediately surrounds the globule.
- d. Lead — a very fusible and very malleable globule. A yellow incrustation is simultaneously produced.
- e. Silver — a brilliant, white, malleable globule, produced without incrustation.

Two other common metals, bismuth and antimony, may be reduced to gray metallic globules, but these globules are brittle, and are not liable to be confounded with the malleable globules just described. Bismuth gives a yellow incrustation which resembles that of lead.

Common charcoal is itself very apt to show a grayish incrustation of ash round about the heated assay; this incrustation remains unaltered or increases, when directly exposed to the flame. The student should test each piece of charcoal before the blowpipe flame, in order that he may not imagine a deposit of ash to be an incrustation derived from the substance under examination.

If a distinct globule has been obtained, it must be picked out with a pair of jewellers' tweezers, and pounded on some smooth and hard body to test its malleability. If it is malleable, replace it upon the charcoal at an unused spot, and heat it strongly with the oxidizing flame. Gold and silver globules fuse, but maintain their brilliancy and give no in-

crustation; this proof distinguishes a genuine gold globule from a yellow globule composed of an alloy of copper and some white metal. A yellow globule composed of oxidizable metals tarnishes instantly in the oxidizing flame. A tin globule fuses, but its bright surface is instantly tarnished, and a white incrustation of binoxide of tin is produced which cannot be driven off by either flame. A lead globule is rapidly converted into litharge, a yellow incrustation being produced, which volatilizes with a bluish color when touched with the reducing flame. A copper globule is blackened by the formation of oxide of copper, and the blowpipe flame is tinged with green.

Certain other phenomena may manifest themselves during this experiment for the reduction of malleable metallic globules. Sulphur, ammonium salts in general, the chlorides, bromides, iodides and sulphides of sodium and potassium, the chlorides of lead, bismuth, tin and copper, metallic mercury, arsenic, antimony and zinc, and many compounds of these four elements, are liable to pass off in vapors, which are often in part deposited upon the coal at a greater or less distance from the hot assay according to their volatility. With the exception of sulphur, these sublimates are white, but when deposited in a thin film upon the black coal they have a gray or blue appearance. During the production of the arsenic sublimate a peculiar odor is evolved; this sublimate being very volatile is only deposited at a considerable distance from the assay. The incrustation produced by zinc is distinctly yellow while hot, but turns white on cooling; it settles near the assay and is driven away again with difficulty. Nitrates and chlorates generally give warning of their presence when heated on charcoal by causing deflagration.

These phenomena, with the exception of the reaction of the nitrates and chlorates, are of secondary importance; the main object of the experiment is the reduction of the five malleable metals above enumerated. We may thus obtain knowledge of the presence of gold (for a confirmatory test,

see § 96, *b*), a metal not included in our scheme of analysis in the wet way. Tin generally gives warning of its presence during this experiment; and this warning is of use, because it is inconvenient to apply nitric acid as a solvent to a substance containing tin, since this reagent converts tin into the very insoluble binoxide of tin. The detection of copper at this stage is of little advantage. The most important fact deducible from the reduction test is the presence of either silver or lead. In dissolving an unknown substance which proves to be insoluble in water, it is customary to try, as the second solvent, chlorhydric acid. The chlorides of silver and lead being insoluble, or difficultly soluble, this acid should not be used as a solvent when either of these two metals is present. Nitric acid must be used instead. Moreover, if the substance has already given evidence of the presence of organic matter (§ 80), porcelain, and not platinum, must be used as a support in destroying the organic matter, as described in the next section, whenever an easily reducible metal is present.

82. Destruction of the Organic Matter. — As already stated in § 80, the presence of fixed organic matter interferes with the detection of many substances, and it must be destroyed before the analysis can be proceeded with. A portion of the original substance, sufficient for the regular course of examination for the metallic elements, is ignited in a porcelain crucible, with free access of air, or better, on platinum foil, if the absence of any easily reducible metal has been proved by the reduction test, until all the carbon is burnt out of it. This ignition is best performed on successive small portions rather than on a large mass at once.

It is obvious that some inorganic volatile matters may be lost during this ignition. Furthermore, some substances, especially alumina and chromic and ferric oxides, are made very insoluble by ignition. Exceptionally, therefore, the following process, which is not liable to these objections, is employed: — The substance in powder, paste or concentrated

solution, is heated in an evaporating-dish, with strong nitric acid, to a temperature just below boiling. To this hot mixture chlorate of potassium, in small bits, is added gradually during several minutes or until the organic matter is all destroyed. The solution is then evaporated to dryness on a water-bath; the dry residue is moistened with strong chlorhydric acid, the mixture diluted with water, warmed, and filtered, if there be any residue. The filtrate is fit for the regular course of analysis, except that potassium, having been added, must not be tested for in this liquid. The residue, if any, must be examined for the insoluble chlorides of Class I. This process is simply a combustion at a low temperature.

The only classes of salts, coming within the scope of this manual, which in the closed tube give evidence of the presence of organic matter, are the acetates and tartrates. It will, of course, be necessary to apply the tests for acetic and tartaric acid to a portion of the original substance and not to the solution obtained above. But the student will not forget the statement already made in § 80, that the presence of organic matter does not necessarily imply the presence of either acetates or tartrates.

B. DISSOLVING A SALT, MINERAL, OR OTHER NON-METALLIC SOLID, FREE FROM ORGANIC MATTER.

83. Before a solid substance can be submitted to the systematic course of analysis, it must be brought into solution. There is no universal solvent. Different substances require different solvents. The four solvents employed in qualitative analysis for salts, minerals, and other non-metallic solids, are water, chlorhydric acid, nitric acid and aqua regia; and these four liquids are to be tried in the precise order in which they here stand. Water is always to be tried first; to whatever resists water, strong chlorhydric acid is applied; if chlorhydric acid fails to dissolve the solid completely, nitric acid is tried, and after nitric acid, aqua regia

as the last resort. If for reasons stated in § 81, the preliminary examination has shown chlorhydric acid to be unsuitable as a solvent, nitric acid is tried immediately after water, and lastly aqua regia as before. A solid substance should invariably be reduced to a very fine powder, before being submitted to the action of solvents (App., § 91).

84. Dissolving in Water. — About half a thimbleful of the powdered substance is boiled with ten times as much water in a test-tube. If an effervescence occurs, as is possible with mixtures containing an acid salt (yeast-powders, for example), the gas evolved should be carefully tested (§ 56-61). If the substance dissolves completely, the solution is ready for analysis. When undissolved powder remains in the tube after protracted boiling, filter a few drops of the liquid, and evaporate a drop or two of the filtrate to dryness on clean platinum foil, at as low a heat as possible. If there be no residue on the foil, or if the residue be scarcely appreciable, the substance is practically insoluble in water, and acids must be tried as solvents. But if, on the contrary, a tolerable residue remains on the foil, decant the liquid in the tube into the filter, and boil the powder again with water. Persevere with this treatment until it is evident that a part of the powder is insoluble in water. The insoluble residue in the test-tube is filtered off; the clear filtrates, collected together and concentrated by evaporation if of unreasonable bulk, are to be labelled " H_2O Sol." and reserved for the regular course of analysis (§ 86). In this case, and in the still more favorable case in which all the substance has dissolved in water, it is a simple aqueous solution which is submitted to analysis.

85. Dissolving in Acids. — The substance which water has failed to dissolve, either in whole or in part, is next boiled in a small dish with three or four times its bulk of concentrated chlorhydric acid, *unless* the tube test (§ 80) or the reduction test (§ 81) has proved the presence of silver, lead or mercury; in which case nitric acid is the first acid to be tried.

If an effervescence occur, the escaping gas is to be tested, as described in §§ 56-61. (See also the last part of § 76a.) After boiling the powdered substance with the strong acid, dilute the fluid with twice its bulk of water, and repeat the boiling if any residue remain undissolved. The acid is diluted because, though the substance to be dissolved is best attacked in the first instance by strong acid, the salts formed by the action of the concentrated acid are more likely to dissolve readily in a dilute than in a strongly acid liquor. Not a few salts which scarcely dissolve in strong acids, are readily soluble in the same acids when diluted. If the whole of the substance finally dissolves, the solution still farther diluted is ready for the transmission of sulphuretted hydrogen (§ 20), for it is of course unnecessary to examine it for members of Class I. If, on the contrary, an undissolved residue remain in the tube, ascertain if anything has dissolved, by carefully evaporating two or three drops of the fluid to dryness on platinum foil. Should an appreciable residue, in excess of that given by two or three drops of the acid employed, remain upon the foil, separate the liquid in the tube from the undissolved substance by decantation or filtration. Reserve the solution, labelling it "**HCl Sol.**"

Rinse the undissolved powder with water, and then boil it in an evaporating dish with three or four times its bulk of strong nitric acid. If the original substance contains silver, lead or a mercurous salt, chlorhydric acid will not have been used, and it will be the residue from the aqueous solution, which is now to be boiled with nitric acid. In this case, effervescence is to be watched for. If the substance dissolves completely in the strong acid, or dissolves, with the exception of a light yellow mass of sulphur, which often separates from a sulphide, evaporate the liquid to a very small bulk to drive off the free acid, dilute the evaporated solution with several times its bulk of water, separate the sulphur, if necessary, by filtration, and reserve the solution, labelling it "**HNO₃ Sol.**" If the substance does not completely dissolve in the strong

acid, dilute the fluid with twice its bulk of water, and repeat the boiling. If the dilute nitric acid effects complete solution, reserve the solution, labelling it as before, "**HNO₃** Sol." If neither the strong nor the diluted nitric acid effects the complete solution of the substance, ascertain if anything has dissolved in the dilute acid by the usual test on platinum foil. If an appreciable residue remain on the foil, separate the undissolved solid in the dish from the liquid by decantation or filtration, and reserve the solution.

Boil the powder, which has resisted both acids taken singly, with aqua regia. If it dissolves completely, evaporate the solution to a very small bulk, dilute the evaporated solution largely with water, and reserve it for analysis, labelling it "Aq. Reg. Sol." It is useless to look for members of Class I in such a solution. If, on the contrary, it does not completely dissolve after protracted boiling, test the liquor to see if anything has dissolved. If an appreciable residue remains on the foil, dilute the acid fluid, filter it, reserve the solution labelled as before, and wash the undissolved residue thoroughly with water, to prepare it for further treatment (§ 86).

Certain silicates, when boiled with concentrated acids, are decomposed, and gelatinous silicic acid is separated. This happens but rarely, however, in the rapid processes of qualitative analysis; and if it should happen, it is not likely to lead the student into error. A residue insoluble in all acids will remain; this residue is, or contains, free silicic acid.

It must not be supposed that it is common to try all four solvents on one and the same substance. Water and chlorhydric acid are the common solvents; nitric acid and aqua regia are, actually, but seldom resorted to as solvents, except for metals (§ 96). It would require some ingenuity to devise an artificial mixture which would put to the test all the capabilities of the above-described method of bringing solids into solution in water and acids. Such mixtures are not met with in ordinary experience. It is the object of any method of analysis to meet real problems, not artificial complications which may be imagined but which do not occur in fact.

C. TREATMENT OF THE SOLUTIONS OBTAINED.

86. Since substances which prove to be insoluble in water and in acids must be brought into solution by peculiar methods, we proceed to consider first the treatment of the solutions already obtained.

I. An Aqueous Solution.—If the student is assured that the unknown substance is a simple salt, he may draw some trustworthy inferences from the fact that the substance dissolves in water. Of the salts which fall within the scope of this manual, the following are practically soluble in water :

1. *All* salts of sodium, and all of potassium and ammonium, except their double platinum-chlorides.
2. *All* nitrates, chlorates and acetates.
3. Chlorides, bromides and iodides, except those of silver and mercury, and the double platinum-chlorides of potassium and ammonium. (Mercuric chloride is soluble. The lead salts are difficultly soluble).
4. Sulphates, except those of barium, strontium and lead.
5. Many hyposulphites.
6. The sulphides of sodium, potassium, ammonium, magnesium, barium, strontium and calcium.
7. A few cyanides, oxalates, tartrates and chromates, besides those of the alkali-metals already mentioned.

It is obvious that any element of the thirty-six considered in this treatise, may be present in an aqueous solution ; but it is also evident from the above list, that a great number of salts are absolutely excluded because of their insolubility in water.

If, on the contrary, there is no certainty that the substance under examination is not a complex artificial mixture, few conclusions can be safely drawn from the fact that a part of it or the whole of it dissolves in water.

Test the solution with litmus paper. The solution is either neutral, acid, or alkaline.

a. The solution is neutral.—The normal salts of most of the metals have an acid reaction. Sodium, potassium, barium, strontium, calcium, magnesium, manganese and silver, are the only metallic elements which form salts whose solutions are neutral. Add to two or three drops of the solution a drop or two of carbonate of sodium. If a precipitate forms, any of the above mentioned elements may be present, and are to be tested for in regular course according to the methods of Part I; if no precipitation ensues, only sodium and potassium can be present, and they may be tested for directly, as described in Chap. VIII.

b. The solution is acid.—The acidity may be caused by a normal salt having an acid reaction, or by an acid salt. Neither carbonates nor sulphides can be present in an aqueous solution with an acid reaction. The solution is to be tested for the metallic elements in the usual manner.

c. The solution is alkaline.—The alkalinity may be due to the hydrates, sulphides, cyanides, or carbonates, of the metals belonging to classes VI and VII; to the presence of a borate, silicate, phosphate, arseniate or aluminate of sodium or potassium; to free ammonia or to carbonate of ammonium. If the alkalinity proceed from an alkaline sulphide, the metals whose sulphides are insoluble in water and in alkaline sulphides, must be absent. If it is due to the presence of the hydrates or carbonates of the metals of classes VI and VII, a very large number of substances are excluded. If it proceed from ammonia or carbonate of ammonium, all substances precipitable by these reagents are absent.

An alkaline solution may obviously contain some substance, soluble in an alkaline solvent like caustic soda or sulphhydrate of ammonium, but liable to immediate precipitation when this solvent is destroyed by the addition of chlorhydric acid at the first step of the analysis. Thus any sulphide of Class III dissolved in caustic soda or in an alkaline sulphide, or compounds of alkaline hydrates with the hydrates of aluminum, zinc or chromium, would be precipitated when the alkaline

solvent was neutralized. Again, the alkaline solution of a silicate of sodium or potassium, when neutralized with acid, yields a very gelatinous whitish precipitate of hydrated silicic acid. From a very concentrated solution of a borate, boracic acid separates in colorless, shining, flat crystals, when the solution is acidified with chlorhydric acid; but the boracic acid thus separated dissolves when the solution is diluted. Again, (although, of course, this could not happen in the case of an alkaline solution actually made by dissolving a solid substance in water) chloride of silver dissolved in ammonia-water would be thrown down by any acid added in excess to the solution. (§ 17, page 19.)

In view of these possibilities, an alkaline aqueous solution should be carefully neutralized with nitric acid, as a preliminary measure, before chlorhydric acid is added to it. Effervescence should be watched for, and, if it occurs, studied as directed in §§ 56-61. Several different cases of precipitation may be distinguished, requiring somewhat different treatment.

a. If the characteristic gelatinous precipitate of silicic acid appears, the acidulated solution must be evaporated to dryness and ignited. The silicic acid is thus rendered insoluble. The ignited residue is digested with dilute nitric acid and filtered. The filtrate is ready for the usual course of analysis. The insoluble residue is silicic acid.

b. If the glistening, colorless plates of boracic acid appear, dilution with warm water will cause them to redissolve.

c. If a precipitate appear on neutralization, whose color or texture proves that it is neither silicic nor boracic acid, but some substance insoluble in water and dilute acids, thrown down in consequence of the destruction of its alkaline solvent, the liquid is made slightly acid and then filtered. The filtrate is ready for the usual course of analysis. The precipitate, rinsed with a little water, is reserved for further treatment; it is not properly a substance soluble in water, and it must be brought into solution by other methods, here-

after to be described. Sometimes a precipitate forms on exact neutralization of an alkaline fluid, which redissolves when the acid is added in excess.

II. An acid solution. — Of the three kinds of acid solutions described in § 85, any one, any two, or all three, may be obtained from a single mixture of different solids. There is an advantage in knowing that a part of a complex mixture is soluble in water, a part in chlorhydric acid, a part in nitric acid and a part only in aqua regia; because this knowledge may enable the student, when he has found out all the elements of the mixture, to make a more probable guess at the manner of their combination in the original mixture, than he would otherwise be able to. But it is quite unnecessary to keep the three kinds of acid solution apart, when all three have been obtained, and to analyze them separately. On the contrary, all three should be mixed together, and analyzed in one course of testing. It must only be borne in mind that when lead, silver, or mercurous salts are present, the nitric acid solution of the residue from the aqueous solution, will give a precipitate of the insoluble chlorides of Class I, on being mixed with a chlorhydric acid or aqua regia solution.

The student must be careful to use no more acid than is absolutely essential. Nitric acid, particularly, is very objectionable; because when free it reacts upon sulphuretted hydrogen with mutual decomposition, sulphur being set free. It has, therefore, been already prescribed to remove the greater part of the free acid by evaporation. Sometimes a strongly acid solution becomes turbid when merely diluted with water. This phenomenon points to the presence of bismuth or antimony. The turbidity will disappear again on the addition of chlorhydric acid.

The mixed acid solutions, after the filtration from any precipitated chlorides of Class I, as first mentioned, are submitted to the regular course of analysis for the metallic elements.

87. Examination of the Solutions for the non-metallic Elements. — As has been already stated in § 45, the

examination for the non-metallic elements invariably follows that for the metallic elements. The method of procedure is usually as follows: If the substance is soluble in water and there is reason to believe that it is not a complex artificial mixture, but a simple substance, the determination of the metallic element generally proclaims the absence of certain classes of salts, so that it is very seldom necessary to apply more than the barium and the silver tests and a few special tests. This will best be illustrated by taking two examples.

Suppose a homogeneous solid, which dissolves readily in water, and which proves to contain strontium. Of the classes of salts coming within the range of this manual (see p. 65), only the sulphide, chloride, bromide, iodide, cyanide, nitrate, chlorate and acetate of strontium are soluble in water; the presence or absence of a sulphide (and probably of a cyanide) will have been shown when chlorhydric acid was added to precipitate the members of Class I; the silver test will show either the presence or absence of the chloride, bromide, iodide and cyanide, and these various classes of salts, if any are present, must be distinguished by special tests; special tests must also be applied for nitrates and chlorates and also for acetates if the substance blackened in the closed tube. In this case, then, the silver test is the only general test necessary, and the number of special tests could hardly be more than four or five.

Again, suppose the substance soluble in water proves to contain a mercurous salt, the only classes of salts to be sought for would be the sulphate (to be decided by the barium test), the cyanide, chlorate, nitrate and acetate (to be determined by special test).

If the only metallic element found in an aqueous solution were sodium or potassium (or the radical ammonium), it would be necessary to look for all the classes of salts enumerated on page 65. In this case the barium test would be applied first, then the silver test, then such special tests as had not been rendered unnecessary by negative evidence.

obtained from the general tests. The calcium test would also be applied if the barium test had made the presence of an oxalate, tartrate or fluoride not impossible.

In the case of an acid solution the conclusions to be drawn from the presence of certain metallic elements are not so general, still in the case of simple substances the absence of certain classes of salts will generally be made sure. For example, a substance under examination, presumptively a simple salt, proves to be insoluble in water, soluble in chlorhydric acid and to contain nickel. The sulphate, chloride, borate, chromate, bromide, iodide, chlorate, acetate and nitrate of nickel are soluble in water and for this reason are excluded from consideration; the sulphite, hyposulphite, sulphide, arseniate, arsenite and carbonate would have revealed themselves in the course of the examination for the metallic elements, and the only salts to be specially tested for at this point are the phosphate, oxalate, tartrate and silicate. If the general and special tests fail to indicate the presence of any of the classes of salts mentioned on page 65, the substance may be an oxide or hydrate. The hydrates give off water when heated in a closed tube; peroxides sometimes give off oxygen under the same conditions, and most oxides when mixed with an excess of carbon, and heated, give off carbonic oxide, or carbonic acid; these gases may be recognized as stated on page 80 under oxalates.

It is evident from what has just been said, that a knowledge of the solubility of chemical compounds is of great value in determining the presence or absence of various classes of salts. The student of qualitative analysis should always have at hand a copy of some work on general chemistry to which he can turn; but for convenience of reference, a table will be found on pages 108, 109, in which are stated in a general way the solubilities of the more commonly occurring salts.

It is to be distinctly borne in mind that this table is not exhaustive, and is intended merely as a help to the beginner,

TABLE OF

	Al ₃ [NH ₄]	Sb	As	Ba	Bi	Od	Ca	Cr ₃	Co	Cu	Au	Fe ²⁺	[Fe ³⁺]
Acetate	W ₁	W	U	U	W	W	W	W ₁	W	W ₁	U	W	W ₁
Arsenate	A	W	U	U	(W)	(A)	U	A	A	A	U	A	A
Arsenite	U	W	U	U	(W)	U	U	(W)	U	A	U	A	A
Borate	U	W	U	U	(W)	A	(W)	(W)	A	(W)	(W)	U	A
Bromide	W	W	(W)	(W)	W	(W)	W	W	W	W	W ₄	W	W
Carbonate	U	W	U	U	A	A	A	A	A	A	U	A	A
Chlorate	W	W	U	U	W	U	W	W	U	W	W	U	W
Chloride	W	W	W	A	W	W ₁	W	W	W	W	W	W	W
Chromate	A	W	A	U	A	A	(W)	W	A	A	(W)	U	U
Cyanide	U	W	U	U	(W)	U	(W)	W	A	A	A	W ₆	(A)
Fluoride	I	W	W	W	(W)	W	(W)	I	W	(W)	(W)	U	(W)
Hydrate	A	W	A-I	A	(W)	A	A	(W)	A	A	A	A	A
Hypo-sulphite	U	W	U	U	(W)	U	W	W	U	W	U	U	W
Iodide	W	W	A	(W)	W	A	W	W	W	W	U ₄	A	W
Nitrate	W	W	U	U	W	W ₁	W	W	W	W	W	W	W
Oxalate	A	W	U	U	A	A	A	A	W	A	A	U	A
Oxide	A	W	A	W	W	A	A	(W)	A-I	A	A	A	A
Phosphate	A	W	(W)	U	A	A	A	A	A	A	U	A	A
Silicate	A-I	U	U	U	A-I	U	U	A-I	U	U	A-I	U	(A)-I
Sulphate	W	W	A	U	I	A	W	(W)	W	W	W	U	W
Sulphide	U	W	A	A	W	A	A	W	U	A	A	A	U
Sulphite	W	W	U	U	A	A	A	(W)	A	A	A	U	(W)
Tartrate	W	W	W	U	(W)	A	(W)	(W)	W	W	(W)	U	(W)

Al₃ [NH₄] Sb As Ba Bi Od Ca Cr₃ Co Cu Au Fe²⁺ [Fe³⁺]

In this table W signifies that the substance is readily soluble in water, (W) that the substance is soluble with difficulty in water; A and (A) that the substance is readily or with difficulty dissolved by acids; I that the substance is insoluble in water or acids; U signifies that the compound is either unknown or so uncommon as rarely to be met with.

§ 87 SOLUBILITIES OF CHEMICAL COMPOUNDS. 169

SOLUBILITIES.

Pb	Mg	Mn	[Hg ²⁺] ¹	Hg ²⁺	Ni	Pt	K	Ag	Na	Sr	Sn ⁴⁺	Sn ²⁺	Zn	
W	W	W	(W)	W	W	U	W	(W)	W	W	W	W	W	Acetate
A	A	A	A	A	A	U	W	A	W	(W)	A	A	A	Arsenate
A	A	A	A	A	A	U	W	A	W	A	A	A	U	Arsenite
A	A	(W)	U	U	A	U	W	(W)	W ₂	(W)	A	U	A	Borate
(W)	W	W	A	(W)	W	W	W	(A)	W	W	W	W	W	Bromide
A	A	A	A	A	A	A	W ₂	A	W ₂	A	A	A	A	Carbonate
W	W	U	W	W	W	U	W	W	W	W	W	W	W	Chlorate
(W)	W	W	(A)	W	W	W	W	(A)-I	W	W	W	W	W	Chloride
A	W	U	A	(W)	W	U	W ₂	A	W	(W)	A	A	W	Chromate
A	W	A	U	W	(A)	(A)	W	A	W	U	U	U	A	Cyanide
A	(A)	A	A	W	(W)	W	W	W	W	(W)	W	W	(W)	Fluoride
(W)	A	A	A	A	A	A	W	A	W	(W)	A	A	A	Hydrate
(W)	W	W	U	U	W	U	W	(W)	W	W	W	U	U	Hypo-sulphite
(W)	W	W	A	A	W	I	W	A	W	W	(W)	(W)	W	Iodide
W	W	W	W	W	W	W	W	W	W	W	A	A	W	Nitrate
A	(W)	(W)	A	A	A	W	W ₂	(W)	W	A	A	W	A	Oxalate
A	A	A	A	A	A	A	W	A	W	(W)	A	I	A	Oxide
A	A	A	A	A	A	U	W	A	W	A	A	A	A	Phosphate
U	I	(A)-I	U	U	U	U	W	U	W	A	U	U	A-I	Silicate
I	W	W	W	W	W	W	W ₂	(W)	W	I	W	W	W	Sulphate
A	W	A	A	A	A	A	W	A	W	W	A	A	A	Sulphide
A	(W)	(W)	W	W	A	U	W	A	W	A	W	U	A	Sulphite
A	W	(W)	A	(W)	A	U	W ₂	A	W	W	(W)	A	(W)	Tartrate

Pb Mg Mn [Hg²⁺]¹ Hg²⁺ Ni Pt K Ag Na Sr Sn⁴⁺ Sn²⁺ Zn

- 1 The basic salt is A.
- 2 The acid salt is W.
- 3 The acid salt is (W).
- 4 The -ous salt is A.
- 5 The -ous salt is I.

who is analyzing comparatively simple substances. In the case of complex mixtures the table is of little service. Thus, chloride of silver is designated as I, but it would be easy to mix chloride of silver and chloride of sodium in such proportions that on treatment with water the whole of the mixture would go into solution: so too the chlorides of potassium and platinum are readily soluble in water, each by itself, but the double chloride of these two elements is so insoluble that it is used as a test for potassium (§ 42) and for platinum (§ 96).

D. TREATMENT OF INSOLUBLE SUBSTANCES.

88. The substances of common occurrence which are practically insoluble in water and acids are: —

The sulphates of barium, strontium and lead.

Chloride of silver.

The anhydrous sesquioxides of aluminum, chromium and iron, either native, or the result of intense ignition.

Chrome-iron-ore, a native mineral.

Some aluminates.

Binoxide of tin, native, or the result of ignition.

Silica and many silicates.

Fluoride of calcium (fluor-spar).

Besides the substances included in this list, sulphur and carbon, or graphite, should, perhaps, be mentioned, because they are insoluble; but they will have been detected during the preliminary blowpipe examination, and their presence allowed for. Bromide, iodide and cyanide of silver are decomposed by boiling with aqua regia, and converted into the chloride, so that these substances never appear in their proper form in the final insoluble residue.

89. Substances which resist solution in liquids are generally liquefied by the action of fluxes at a high temperature; they are fused in contact with some powerful decomposing agent, like the carbonate or acid sulphate of an alkali-metal,

or the hydrate or carbonate of an alkaline-earth metal. Certain preliminary experiments should precede the fusion.

The insoluble powder is first examined carefully (with the help of a lens, if convenient) to ascertain if it is a homogeneous substance of the same color throughout, or a mixture composed of dissimilar, variously-colored particles. The following blowpipe experiments sometimes give decisive indications, particularly with homogeneous substances.

a. The reduction test (§ 81) is repeated with great care, looking especially for silver, lead and tin, and applying to the globule, if any is obtained, the test for distinguishing between these three white metals. This test has already been applied to the original substance; but if this substance was a complex mixture containing soluble ingredients, it is quite possible that the test should give a more satisfactory result, now that all substances soluble in water and acids have been removed, than it yielded before. If, however, decided indications of the presence of a reducible metal were obtained in the first instance, the repetition of the test is, of course, unnecessary. If *any* reducible metal is detected, it is necessary to use a porcelain crucible for the fusion which it may be desirable to make (§ 90) in order to convert the insoluble substance into a more manageable form. A platinum crucible, which is employed for most fusions, cannot be used with safety when the substance to be fused contains any reducible metal; for many of the alloys of platinum are extremely fusible.

Sometimes, when the substance under examination contains but a small proportion of metal, some metal may be reduced during the blowpipe experiment on charcoal, but the detached particles may not run together into a single conspicuous globule. Since a mistake as to the presence of a reducible metal may involve the destruction of a platinum crucible, it is best in doubtful cases to operate in a more delicate fashion. To ascertain, beyond question, whether any reduced metal has been separated in this experiment, moisten the cavity in the

charcoal with water after the fusion has been finished, cut the charcoal out for a little distance, both around and below the cavity, and transfer the contents of the cavity and the scraps of charcoal to an agate or porcelain mortar. Pulverize the whole mass, and then carefully wash away the powdered charcoal and all the lighter portion of the mixture. Any malleable metal that may have been reduced remains in the mortar in little flattened grains or spangles, in which the peculiar color and lustre of the metal or alloy are generally visible. Sometimes metallic streaks are produced on the mortar or pestle by little particles of metal ground between them. The student must not mistake glistening particles of wet charcoal sticking to the mortar or pestle for metallic spangles, and the metal should be thoroughly removed from both mortar and pestle by the use of a few drops of warm aqua regia, immediately after the experiment is finished, in order to avoid errors on a subsequent occasion.

b. Prepare another pellet of a mixture of equal parts of the insoluble powder and carbonate of sodium, adding a little charcoal powder to the paste. Fuse this mixture upon charcoal in the reducing flame of the blowpipe. Scoop out the fused mass and the surrounding charcoal with a penknife, place the dry mass upon a bright surface of silver (coin or foil), and wet it with a drop of water. If a brown stain be produced on the silver, it is evidence of the presence of sulphide of sodium in the fused mass. This sulphide results from the reduction of a sulphate, and is evidence of the presence of a sulphate in the substance tested. The odor of sulphuretted hydrogen is often perceptible when the fused mass is moistened. The silver coin or foil may be replaced by a piece of lead paper, if care be taken not to mistake the mere dirtying of the paper for a stain of sulphide; the silver is, however, to be preferred; it may be cleaned after use by treating it with a solution of cyanide of potassium and then washing with water. It is obvious that the carbonate of sodium used in this test must be so free from sulphate of

sodium as not itself to give this reaction on silver, after fusion on charcoal. Since coal-gas invariably contains traces of sulphur compounds, the test cannot be performed with a gas-flame; a candle or lamp flame (App., § 78) must be employed.

It is, of course, possible to apply this test for sulphates to the fused mass obtained in (a); this second test is in fact unnecessary when a decided reaction has been obtained in the first instance.

c. Make the loop on the end of the bit of platinum wire (App., § 79) white-hot in the blowpipe flame, and thrust it white-hot into some powdered borax; a quantity of borax will adhere to the hot wire; reheat the loop in the oxidizing flame; the borax will puff up at first, and then fuse to a transparent glass. If enough borax to form a solid, transparent bead within the loop does not adhere to the hot wire the first time, the hot loop may be dipped a second time into the powdered borax.

When a transparent glass has been formed within the loop of the platinum wire, touch the bead of glass while it is hot and soft, to a few particles of the insoluble powder, and reheat the bead with the adhering powder in the oxidizing flame. If the substance dissolves slowly in the borax, and the bead has a fine yellowish-green color when cold, chromium is probably present. Reheat the bead in the reducing flame: if it presents a bright green color both when hot and cold, there is no doubt of the presence of chromium.

It sometimes happens when too much of the substance to be tested has been added, that the borax bead becomes so dark-colored as to be practically opaque. It may then be flattened while soft, by sudden pressure between any smooth metallic surfaces, like the flat parts of jewellers' tweezers. If the flattening makes the color of the borax-glass visible, nothing more is necessary; but if the glass is still too dark, all the glass outside the loop of platinum may be broken off by gentle hammering, and the remaining glass may be reheated and largely diluted by the addition of more borax.

It is convenient to be informed of the presence of chromium, because chromic oxide and chrome-iron-ore are substances which it is particularly difficult to decompose effectually by fusion. In presence of chromium, no other bead-reaction which can be anticipated under the circumstances will give a decisive result; but in the absence of chromium, the presence of iron may be determined. A suitable quantity of oxide of iron causes the borax-bead, heated in the oxidizing flame, to look red when hot and yellow when cold. In the reducing flame the iron bead becomes greenish, or light brownish-green.

This test is rendered unnecessary if the substance under examination be a white powder, or if from other appearances the absence of chromium is assured.

d. The test for fluorine (§ 70) should be applied to the original substance, if it has not already been done.

When all the above-mentioned tests (a-d) give negative results, the simplification of the problem is very conspicuous; the substances which may be present are reduced to alumina and some aluminates, silica and silicates. Again, in the case of a substance evidently homogeneous, if the preliminary tests give affirmative results, the indications of the character of the substance are almost conclusive. Thus chloride of silver, sulphate of lead, chromic or ferric oxide, binoxide of iron, or fluoride of calcium, may be satisfactorily identified by the preliminary tests alone.

There are two methods of changing insoluble substances into more manageable forms by the application of heat with sufficient exactness for the purposes of the qualitative analyst, — the method by fusion, and the method by deflagration.

90. Fusions.—Mix the fine powder of the insoluble substance with about six parts by weight of dry carbonate of sodium in powder. Both powders must be as fine as they can be made, and they must be intimately mixed. Keep the mixture at a bright red heat, in a platinum crucible (a *porcelain*

crucible, if a reducible metal has been found in the substance, § 89, a, and fusion is for any reason preferred to deflagration) until the mass has been brought to a state of quiet fusion (App., § 75). Place the hot platinum crucible, when withdrawn from the lamp or fire, on a cold block, or thick plate of iron, and let it cool. If a gas blast-lamp be employed, the supply of gas may be interrupted, and the blast of air, directed as before, upon the crucible, until it has become cold.

When the green borax bead, and the dark color of the insoluble powder, point to the presence of chrome-iron-ore, a mixture of three parts, by weight, of carbonate of sodium with three parts, by weight, of nitre, may be substituted for the six parts of carbonate of sodium alone.

91. Treatment of the Fused Mass. — When the crucible has been cooled in the way mentioned above, the fused mass can generally be removed from the crucible in an unbroken lump. Soak the lump in boiling water until everything is dissolved which is soluble in water. If the mass cannot be detached from the crucible, the crucible and its contents must be soaked in boiling water.

The aqueous solution of the fused mass is filtered from the residue insoluble in water and reserved. That portion of the fused mass which boiling water did not dissolve is treated with acid, — chlorhydric acid if silver and lead be absent, nitric acid if either of these metals be present, — and the acid solution obtained is treated as will be described. If a portion of the fused mass resist both water and acids, the insoluble portion may consist of separated silicic acid, or of some of the original substance undecomposed by the fusion. In the latter case, another and more prolonged fusion is the only effectual remedy, although it may often happen that a partial decomposition of the insoluble substance will enable the analyst to recognize all the elements which it contains.

The treatment of the aqueous and acid solutions of the last paragraph will be best understood if we first consider what

changes take place in the process of fusion. Suppose that the substance in hand is sulphate of barium; at the high temperature of the fusion the barium and sodium change places and, instead of sulphate of barium and carbonate of sodium, there result carbonate of barium and sulphate of sodium: $\text{BaSO}_4 + \text{NaCO}_3 = \text{NaSO}_4 + \text{BaCO}_3$. When the fused mass is treated with water, the sulphate of sodium (with the excess of carbonate of sodium) goes into solution, while the carbonate of barium, which is insoluble in water, is dissolved by the chlorhydric (or nitric) acid as chloride (or nitrate) of barium. Therefore in a case like this, the metallic element would be found in the acid solution and the *class* or *kind* of salt might be determined by applying the test for sulphates to the aqueous solution. Again, suppose the substance under examination is a double silicate of calcium and aluminum. After fusion with carbonate of sodium and treatment successively with water and acid, a portion of the silicic acid will be in the aqueous solution (as silicate of sodium) and a portion in the acid solution, while a part may remain insoluble; the aluminum will exist partly in the aqueous solution (as aluminate of sodium) and partly in the acid solution (as chloride of aluminum); the calcium, which after the fusion remained as carbonate, insoluble in water, will have been converted into chloride and will be found in the acid solution. Having considered the general nature of the changes brought about by fusion with carbonate of sodium, we proceed to the statement of the treatment of the aqueous and acid solutions of the fused mass

a. If the test for sulphates described in § 89, b, on page 112, has failed to give satisfactory indications, acidify a small portion of the aqueous solution with chlorhydric acid, and apply the barium test. The carbonate of sodium used in the fusion should be free from sulphate.

b. Acidify another small portion with acetic acid, and apply the lead test for chromates (§ 62). In presence of sulphuric acid this test will be obscured, but not rendered wholly useless (§ 30, p. 40).

c. Acidify a third portion with nitric acid, and apply the silver test for chlorine. The student must first prove that his carbonate of sodium contains no chloride.

d. If the test for fluorine by the method of § 68 has, for any reason, been unsatisfactory, a fourth portion, having been concentrated by evaporation in a porcelain dish, and again cooled, is acidified with chlorhydric acid, and then left at rest until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, and filtered while hot. The filtrate is collected in a bottle; chloride of calcium is immediately added to it; the bottle is closed and allowed to stand at rest. If the original substance contained a fluoride, the fluorine will have combined with sodium during the fusion, and fluoride of sodium will be contained in the aqueous solution. The carbonic acid having been expelled, and all substances precipitable by ammonia having been removed, the chloride of calcium will throw down the fluoride of calcium. If a precipitate separates from the liquid in the bottle after some time, it is collected in a small filter, dried and examined for fluorine by the method of § 68.

When the tests a-d give negative results, or when by previous tests the absence of sulphates, chromates, chlorides and fluorides is made certain, the remainder of the aqueous solution is added to the acid solution and the mixture is evaporated to dryness and ignited; the residue thus obtained is boiled with dilute chlorhydric (or nitric) acid. If the dilute acid fails to dissolve the residue completely, the insoluble portion consists of silicic acid. The solution is examined in the usual way for the metallic elements (§ 44), except, of course, sodium (and sometimes potassium), which has been added in the flux. (See § 92, p. 118).

When the preliminary examination or the tests a-d show the presence of one or more of the classes of salts mentioned above, the treatment is slightly different. In that case the remainder of the aqueous solution is acidified with chlorhydric acid, evaporated to dryness and ignited; the residue

thus obtained is boiled with dilute chlorhydric acid. If the acid fails to dissolve the residue completely, the insoluble portion consists of silicic acid; the solution may be tested for aluminum. (See page 116.) If silicic acid has been found in the aqueous solution, the original acid solution of the fused mass is evaporated to dryness and ignited; the residue is treated with dilute acid, and the solution after being filtered from the silicic acid is examined for the metallic elements in the usual manner. It is evidently impracticable in this last case to mix the aqueous and the acid solutions, for if the case of sulphate of barium (p. 116) be taken as an example, in mixing the aqueous solution (containing sulphate of sodium) and the acid solution (containing chloride of barium), there would be an immediate precipitation of the insoluble sulphate of barium which was the substance to be analyzed.

Silicates are by far the most common of insoluble substances. A great variety of metallic elements occur in insoluble silicious minerals, so that the possible contents of the acid solution of the fused mass are very various. The evaporation to dryness in order to render the silica insoluble is prescribed because the subsequent examination goes on the better for this preliminary removal of silica, which, if left in solution, might create confusion by appearing as a precipitate at almost any stage of the analysis.

Many silicates contain sodium and potassium. When the presence or absence of these alkali-metals is to be determined, it is evident that the pulverized silicate must not be fused with carbonate of sodium, but with some decomposing flux free from alkali.

92. Decomposition by Means of Carbonate of Calcium and Chloride of Ammonium. — An intimate mixture is prepared of one part of the silicate, six parts of pure precipitated carbonate of calcium, three fourths part of pulverized chloride of ammonium. This mixture is heated to bright redness in a platinum crucible for thirty or forty minutes. The crucible with its contents (which should be in a

coherent, sintered, but not thoroughly fused condition), is then placed in a beaker, and soaked for half an hour in water kept near the boiling point. The contents of the beaker are then filtered. The filtrate, containing caustic lime, chloride of calcium, and all the sodium and potassium of the original silicate as chlorides, is treated with a little ammonia-water, and with carbonate of ammonium in slight excess; the liquid is heated to boiling and filtered. This second filtrate is evaporated to dryness, and gently ignited to expel the ammonium salts. The residue is dissolved in a little water; one or two drops of carbonate of ammonium, and a drop of oxalate of ammonium are then added; the mixture is again heated and filtered; this third filtrate is evaporated to dryness and ignited; the ignited residue, if there be any, consists of the chlorides of sodium and potassium, or of one of these two salts. This residue is examined according to § 42.

93. Fusion with Acid Sulphate of Sodium. — The following method may be tried to advantage upon ferric oxide, chromic oxide, or chrome-iron-ore, and some very refractory silicates. Heat the insoluble substance with three or four times its bulk of acid sulphate of sodium (App., § 29) in a platinum crucible, until the sulphate melts; then maintain it in the liquid state for half an hour. This operation should be performed under a hood. The fused mass is treated essentially as before (§ 91), allowance being made for the different nature of the flux.

94. Deflagration. — The method of fusion just described involves the use of a platinum or porcelain crucible, and demands the heat of a blast-lamp, or strong coal fire. Neither crucibles, lamps nor fires are necessary in the method of deflagration, which applies the heat inside the mass to be fused. This decomposition by deflagration is performed as follows: One part, by weight, of the insoluble powder is intimately mixed with two parts of dry carbonate of sodium, two parts of fine and pure charcoal powder, and twelve parts

of powdered nitre. The mixture is put in a thin porcelain dish or clean iron tray; the dish, or little tray, is placed under a hood, or in the open air, and a lighted match is applied to the centre of the heap. The deflagration is completed in two or three seconds, and a well-fused mass remains. This mass is detached from the cooled dish or tray, and boiled with water in a beaker; it is generally very porous, and is therefore readily disintegrated by stirring it in the hot water with a glass rod. The soluble portion will all be extracted in a very few minutes. The residue left by water is treated with acid precisely as described in § 91. The aqueous and acid solutions of the deflagrated substance are submitted to the same operations as the corresponding solutions of substances fused in crucibles. A little charcoal is generally left undissolved by the acid, and with it any of the substance which may have escaped decomposition. The mixture of one part, by weight, of powdered charcoal, and six parts of nitre, may be kept ready mixed for effecting the fusion of insoluble substances.

The advantages of this process are that it is quick, requires only cheap and common tools, and may be applied to substances containing reducible metals, as well as to any others. It is, of course, inapplicable when sodium and potassium are to be sought for in silicates. Chrome-iron ore cannot be decomposed in this way. The insoluble sulphates, chloride of silver, binioxide of tin, fluorspar, glass, and many natural silicates, may be very well treated by this method, in spite of its apparent roughness.

CHAPTER XII.

TREATMENT OF A PURE METAL OR ALLOY.

95. THE elements which are now used in the arts in the metallic state, and which therefore may come into the hands of the analyst as metals, either pure or alloyed, are silver, lead, mercury, bismuth, cadmium, copper, arsenic, antimony, tin, gold, platinum, aluminum, iron, zinc, nickel and magnesium. These metals can all be brought into solution and detected in the wet way with ease and certainty. It is therefore not worth while to submit a metal, or metallic alloy, to preliminary blowpipe tests, although at need mercury and arsenic can be readily detected by the closed-tube test (§ 80), and many others, by exposing them on charcoal to the reducing and oxidizing flame (compare § 81, pp. 95-97).

A portion of the metal or alloy to be examined should first be reduced to as fine a state of division as possible. If it is brittle, it can be powdered; if soft, shavings can be cut from it; if tough and hard, it can perhaps be fused, and shaken into powder while melted, or granulated by being poured from a height into cold water. Filings should be the last resort, because of the possibility of foreign admixture of iron.

96. Action of Nitric Acid on the Metals.—A small quantity of the divided metal or alloy, about the equivalent of a pea in bulk, is placed in a flask, covered with concentrated nitric acid, and heated gently under a hood or in the open air for half an hour.

If complete solution ensues, gold, platinum, tin and antimony are probably altogether absent; they can only be present in very minute proportion. Any of the other metals above enumerated may be present. Transfer the acid solu-

tion to a porcelain dish, and evaporate it almost to dryness ; dilute the evaporated liquid with about ten times its bulk of water, and proceed with the analysis in the usual way (§ 44). If the solution, from which the greater part of the free acid has been removed by evaporation, becomes turbid on the addition of water, bismuth is doubtless present. In this case enough acid must be restored to the solution to clarify it. Mercury, if present, will be dissolved to mercuric nitrate.

If a residue remains undissolved, add a little more acid to make sure that the acid is incapable of further action ; and when this point is settled, test a drop or two of the clear liquid on platinum foil, to ascertain if anything has entered into solution. If the nitric acid has effected a partial solution of the original metal, evaporate the liquid nearly to dryness, dilute the evaporated mixture with water, filter, and submit the filtrate to the usual course of analysis. The residue is thoroughly washed with water, to prepare it for further treatment. On diluting the evaporated mixture with water, a turbidity due to the presence of bismuth may appear. The experienced operator will hardly fail to distinguish between any such turbidity and a residue insoluble in the nitric acid. To avoid mistakes which would lead to the unnecessary addition of acid, it is well to take out a drop of the nitric acid solution before evaporation and to add it to several teaspoonfuls of water contained in a test-tube. (See p. 24.) The absence or presence of bismuth will thus be discovered. It will sometimes happen that a white residue appears in the nitric acid solution which disappears when the evaporated mixture is diluted. This is owing to the presence of lead : nitrate of lead is rather insoluble in strong nitric acid but passes into solution readily when the mixture is diluted.

Three different cases of insoluble residues may occur, readily distinguished by the mere appearance of the residue.

a. The insoluble substance is non-metallic and white. In this case tin and antimony may be present, but gold and

platinum are probably absent. The white residue may contain the insoluble oxides of tin and antimony, or either of them. These elements are to be detected by the methods of § 25, or by the method described just below (first part of c).

b. The insoluble substance is metallic, as evidenced by its lustre, if it is in visible fragments, or by the weight and gray or black color of its powder, if it is in a fine state of division. Such a residue must be either gold or platinum (or some of the rare platinum-like metals which lie without the range of this manual). The residue is dissolved in aqua regia, and evaporated to a very small bulk.

Test for Gold. — A portion of this evaporated liquid is diluted with ten times its bulk of water, and poured into a beaker which is placed on a sheet of white paper. A small quantity of a solution of protochloride of tin is tinged yellow by the addition of a few drops of solution of sesquichloride of iron (App., § 48), and then considerably diluted. A glass rod is dipped, first into this tin solution, and then into the solution to be tested for gold. If even a trace of the precious

Test for Au. metal be present, a blue or purple streak will be observed in the track of the rod. If the quantity of gold be more considerable a pink tinge will be imparted to the solution, or a purplish precipitate will be produced by a sufficient quantity of the tin-solution. This "purple-of-Cassius" test is applicable to very acid solutions.

Test for Platinum. — To another undiluted portion of the cooled aqua regia solution, a cold concentrated solution of chloride of ammonium is added. The formation of a yellow, crystalline precipitate of chloroplatinate of ammonium indi-

Test for Pt. cates the presence of platinum (or of some rare platinum-like metal). By adding a little alcohol to the liquid, the test is made more delicate. In a difficult case, the aqua regia solution might be evaporated to dryness with chloride of ammonium, and the residue treated with weak alcohol and water, which would dissolve all the

Ingredients except the chloroplatinate. Upon ignition, chloroplatinate of ammonium leaves spongy platinum behind.

It happens exceptionally in the case of certain alloys, especially in the presence of copper, that *concentrated* nitric acid fails to attack them even when it is hot; it is well, therefore, before inferring the presence of an insoluble metallic residue to try the effect of boiling the seemingly insoluble substance in nitric acid diluted with an equal bulk of water.

c. The insoluble residue contains both a white powder and a metallic substance. It must then be examined for antimony, tin, gold and platinum. The following directions presuppose the presence of all four metals, — a very rare case.

The residue is treated for the detection of antimony and tin, precisely as described in § 25. Gold and platinum remain unchanged in the metallic state through the various operations. After dissolving the tin in chlorhydric acid (page 34, top), the residue is treated again with chlorhydric acid to insure the complete removal of the tin, and is then washed thoroughly by decantation. The washed residue is warmed for a quarter of an hour with a solution of tartaric acid (App., § 13), and a few drops of nitric acid are added towards the close of the digestion. Antimony dissolves in this tartaric acid solution; its presence may be verified by passing sulphuretted hydrogen through the decanted solution. The platinum foil having been taken out of the porcelain dish, the metallic residue from the tartaric acid solution is thoroughly washed by decantation, dissolved in aqua regia, and tested for gold and platinum, as just described in *b*, above.

CHAPTER XIII.

TREATMENT OF LIQUIDS.

97. Evaporation Test.— The first step in the examination of an unknown liquid is to evaporate a few drops at a gentle heat on platinum foil. Attention should be paid to the smell of the escaping vapors in order to ascertain if the solvent be water or some other fluid, like alcohol, ether, benzine, or a strong acid. If no appreciable residue remain, the fluid is probably pure water, or some other volatile liquid; or it is possible that the liquid is some very dilute solution, like a spring water, which needs extreme concentration before the solid substances dissolved in it can be detected. When a residue remains on the foil, the heat is increased, first, to ascertain if the dissolved substances are wholly volatile, in which case only compounds of ammonium, mercury, arsenic and antimony, can be present; and, secondly, to ascertain if there be any organic matter in the liquid. Carbonization or charring with the attendant phenomena (§ 80, I) occurs when fixed organic matter is present. If organic matter is discovered, it must be destroyed by the second method of § 82, before the analysis can be proceeded with. A volatile organic solvent can, of course, be got rid of by a simple evaporation to dryness.

98. Testing with Litmus.— The next step is to test the solution with litmus-paper.

a. If it is neutral, and the solvent is water, consult § 86.

b. If it is acid, the acidity may be due to a normal salt having an acid reaction, or to an acid salt, or to free acid. No general inferences can be drawn from the acid reaction, except that carbonates and sulphides are absent. If dilution

of the acid fluid produces turbidity, the presence of antimony or bismuth may be inferred.

c. If it is alkaline, consult § 83, c.

99. By evaporating a portion of the original solution to dryness, the dissolved solid is obtained. This solid may be subjected to the whole of the preliminary treatment prescribed for a salt, mineral, or other non-metallic solid (§§ 80, 81); but inasmuch as the main object of all preliminary treatment of a solid is to learn how to get it into solution with the least difficulty, it is seldom worth while for the analyst to make a solid out of a solution, and thus forego the advantage of having the solution already made to his hand.

100. Testing for Ammonia. — A small portion of the original solution must always be tested for ammonium salts, by heating it in a test-tube with an equal bulk of slaked lime. The gas is recognized by its smell and its reaction with chlorhydric acid (§ 80, III. b).

The means of identifying and isolating the rare elements, the methods by which minute traces of one substance may be detected when hidden in proportionally large quantities of other substances, as when the impurities of chemicals and drugs are exhibited, and the processes to be employed in special cases of peculiar difficulty, such as the analysis of complex insoluble minerals, or the detection of mineral poisons in masses of organic matter, must be studied in complete treatises upon chemical analysis, or in works specially devoted to these technical matters. Such details, however valuable to the professional analyst, or expert, would not be in harmony with the plan of this manual.

ANOTHER METHOD FOR THE TREATMENT OF CLASS III.

§ 25a. **Analysis of the Mixed Sulphides.**—As considerable difficulty is often experienced, especially by beginners, in analyzing the mixed sulphides of this class, the following method of treatment is suggested as an alternative.

To effect the separation:—Add dilute chlorhydric acid in small portions to the sulphhydrate of sodium solution until the reaction is distinctly acid. The sulphides of arsenic, antimony, and tin, are precipitated, together with some free sulphur. Any large excess of acid is to be avoided lest the sulphides of antimony and tin, which are somewhat soluble in chlorhydric acid, fail to be precipitated.

Collect the precipitate on a filter and throw the filtrate away. The precipitate is rinsed with water, transferred to a test-tube or small flask, covered with strong chlorhydric acid, and gently warmed, *not boiled*. The yellow residue is sulphide of arsenic. The antimony and tin pass into the filtrate as chlorides. To test for these elements, prepare a small hydrogen-generator, as described at the bottom of page 32, and test for the elements as indicated on page 33.

To test for arsenic, transfer the sulphide of arsenic which did not dissolve in the strong chlorhydric acid to a small flask, add a teaspoonful of strong nitric acid, and warm GENTLY for several minutes. Then add in small successive portions chlorate of potassium, using in all an amount no larger than a half-pea.

When the sulphide of arsenic has entirely dissolved, pour the liquid into an evaporating dish and warm *gently* until the chlorous smell has disappeared. This treatment for arsenic must be carried on where there is a good draught, and the acid must be warmed, not boiled. When the chlorous fumes have been driven off, add ammonia-water until the reaction is alkaline, filter, if necessary, and to the clear alkaline liquid

add a small quantity of a prepared solution of sulphate of magnesium and chloride of ammonium, and set the mixture aside for twelve hours. The formation of a white crystalline precipitate of arseniate of ammonium and magnesium is evidence of the presence of arsenic.

APPENDIX.

REAGENTS.

[** Those reagents in the following list, which are marked with the double asterisk, are rarely employed; a single, small bottle of each of them in the laboratory, will be enough for many students. * Those marked with a single asterisk had also better be kept in one or two bottles of sufficient size, rather than be distributed to each student, because of their liability to spoil; several of them are used in considerable quantities.]

HCl. + **1. Chlorhydric Acid (Concentrated).**—The strong common acid prepared by chemical manufacturers, though usually far from pure, will answer for most of the purposes of this manual. It must, however, be continually borne in mind that the commercial acid is usually contaminated with sulphuric acid, and very often with traces of arsenic and iron. These impurities may be present in sufficient quantity to render the acid unfit for use when these very substances are to be tested for in the mixture to be analyzed.

The yellow color of the commercial acid, though often attributed to iron, is really due for the most part to the presence of a peculiar organic compound which is soluble in the strong acid.

If in any experiment doubts arise concerning the character of a reagent, a quantity of it, somewhat larger than that which has been mixed with the substance under examination, should be tested by itself, and the reaction compared with that exhibited in the doubtful case. If the result of this trial is unsatisfactory, the experiment must be repeated with reagents which are known to be pure.

HCl **2. ** Chlorhydric Acid (Pure)** may be prepared by distilling a mixture of fused chloride of sodium and sulphuric acid, and collecting the gas in water. (See Elliot and Storer's Manual of Inorganic Chemistry, Exp. 49.)

HCl + H₂O **3. Chlorhydric Acid (Dilute).**—Mix 1 volume of the com-

mon concentrated acid, or — where special purity is required — of the pure strong acid, with 4 volumes of water.

HNO_3 · 4. **Nitric Acid (Concentrated).** — Use the colorless commercial acid of 1.38 or 1.40 specific gravity. Strong nitric acid of tolerable purity can usually be obtained from the dealers in coarse chemicals. An acid, which when diluted with five parts of water gives no decided cloudiness with either nitrate of silver (absence of chlorhydric acid) or nitrate of barium (absence of sulphuric acid) is good enough for most uses in qualitative analysis.

HNO_3 + ag 5. **Nitric Acid (Dilute).** — Mix 1 volume of the strong acid with 5 volumes of water.

HNO_3 + 3HCl 6. **Aqua regia** should be prepared only in small quantities, at the moment of use, by mixing in a test-tube one volume of *strong* nitric acid, with three or four times as much *strong* chlorhydric acid.

H_2SO_4 · 7. **Sulphuric Acid (Concentrated).** — The oil of vitriol of commerce will usually be found pure enough for the purposes of this manual.

H_2SO_4 8. ** **Sulphuric Acid (Pure).** — Sulphuric acid free from chlorhydric acid is necessary in testing for chlorine according to § 71. Such acid may be obtained from the dealers in fine chemicals, but acid purporting to be pure should invariably be tested by diluting a portion with a considerable quantity of water and adding a few drops of nitrate of silver. No turbidity should appear after the mixture has stood for some time.

H_2SO_4 + ag 9. **Sulphuric Acid (Dilute)** is prepared by gradually adding 1 part by measure of the concentrated acid to 4 parts of water contained in a beaker or porcelain dish; the mixture must be constantly stirred with a glass rod. When the mixing is finished, the liquid is left at rest until all the sulphate of lead, which has separated from the strong acid, has settled to the bottom; the clear liquid is then decanted into bottles.

H_2SO_4 + ag ** 10. **Sulphuric Acid (Dilute)** for the separation of copper and cadmium (p. 25). Mix, as described in the preceding section, 1 part of the strong acid with 5 parts of water.

11. **Oxalic Acid.** — Dissolve 1 part, by weight, of the commercial crystals, in 20 parts of water.

$C_2H_4O_2$ 12. **Acetic Acid.** — The ordinary commercial acid.

13. **Tartaric Acid** should be kept in the state of powder, since solutions of it slowly decompose. For use, dissolve a small portion of the powder in two or three times its volume of hot water.

H_2S 14. **Sulphuretted Hydrogen Gas (Sulphydic Acid)**, is prepared as needed, by acting upon fragments of sulphide of iron with dilute sulphuric acid in the apparatus described in §§ 89, 90 of this Appendix. The apparatus should always be placed either in the open air or in a strong draught beneath a chimney.

$H_2S + ag$ 15. **Sulphuretted Hydrogen Water**. — Pass sulphuretted hydrogen gas into a bottle of water until the water can absorb no more. To determine when the absorption is complete, close the mouth of the bottle tightly with the thumb, and shake the liquid. If the water is saturated, a small portion of the gas will be set free by the agitation, and a slight outward pressure against the thumb will be felt. If the water is not fully saturated, the agitation will enable it to absorb the gas which lay in the upper part of the bottle, and a partial vacuum will be created, so that an inward pressure will be felt.

Since sulphuretted hydrogen water soon decomposes when exposed to the air, it should always be kept in tightly closed bottles, and no very large quantity of it should be prepared at once. A good way of keeping the solution is to fill a number of small phials with the fresh liquid, cork them tightly, and invert them in water, so that their necks shall always be immersed and protected from the atmosphere.

At the moment of using this reagent its quality should always be proved by smelling of it, or by adding a drop or two of the liquid to a drop of acetate of lead, which should be immediately blackened from the formation of sulphide of lead.

$H_2N + ag$ 16. **Ammonia-Water**. — Commercial aqua-ammonia may usually be obtained pure enough for the purposes of this manual. Dilute 1 volume of the strong liquor with 3 volumes of water. Ammonia-water should be free from carbonic acid; when diluted, as above, it ought not to yield any precipitate when tested with lime-water.

H_2NHS 17. ***Sulphydrate of Ammonium**. — Pass sulphuretted hydrogen gas through ammonia-water, diluted as described in § 16, until a portion of the liquid yields no precipitate when tested with a drop of a solution of sulphate of magnesium (absence of free ammonia).

Since sulphydrate of ammonium decomposes after a while, when exposed to the air, it is not advisable to prepare it in large quantities. In case any doubt arise as to the quality of the reagent, add some of it to a drop of acetate of lead. Unless a dense black precipitate of sulphide of lead is immediately thrown down, the sulphydrate is worthless.

$(H_2N)_2CO_2$ 18. **Carbonate of Ammonium**. — Dissolve 1 part, by weight,

of the commercial salt, in 4 parts of water, and add to the mixture 1 part of strong ammonia-water.

The solution of carbonate of ammonium should be kept in bottles made of glass which is free from lead. If kept in flint-glass bottles, the carbonate of ammonium takes up some lead so that when, in precipitating the carbonates of Class VI, this reagent is added to a solution containing sulphhydrate of ammonium, a dark coloration appears in the liquid or obscures the precipitate to the annoyance of the operator.

H₂NCl 19. **Chloride of Ammonium.**— Dissolve 1 part, by weight, of the crystallized commercial salt in 10 parts of water.

20. **Oxalate of Ammonium.**— Dissolve 1 part, by weight, of the salt in 24 parts of water: or, dissolve 37 grms. of crystallized oxalic acid in 450 c. c. of water, neutralize exactly with ammonia-water and dilute to the bulk of 1 litre.

21. **Molybdate of Ammonium.**— Digest 1 part, by weight, of molybdic acid for some hours in 4 or 5 parts of strong ammonia-water, and mix the clear solution with 12 or 15 parts of strong nitric acid; or dissolve 1 part of molybdate of ammonium in 3 or 4 parts of weak ammonia-water, and mix the liquid with 12 or 15 parts of nitric acid, as before.

Na HO 22. **Caustic Soda.**— Place 1 part, by weight, of the best commercial caustic soda in a large, stoppered bottle; pour upon it 8 or 9 parts of water, and shake the bottle at intervals until the whole of the soda has dissolved. Leave the bottle at rest until the liquid has become clear, and finally transfer the solution, with a siphon, to the small bottles in which it is to be kept for use. The solution thus prepared, though pure enough for the uses prescribed in this manual, is really far from pure. It would be unfit for use in a delicate research, because it is usually contaminated with chloride, sulphate and carbonate of sodium, and is liable to contain traces of aluminate, phosphate and silicate of sodium. Since some nitrate of sodium is added to it in the process of manufacture, the soda is liable to be contaminated with this salt and the products of its decomposition, including ammonia. This last impurity is liable to be given off when the solution is boiled.

Caustic potash, as prepared for surgeon's use, may be substituted for caustic soda whenever it can be more readily obtained. The potash should be dissolved in about 10 parts of water.

Since solutions of the caustic alkalies act upon glass rather easily, especially when its outer surface or "fire-glaze" has once been removed, it often happens, when the soda solution is kept in glass.

stoppered bottles, that the stoppers become immovably cemented to the glass by the silicate of sodium which forms in their necks. This difficulty may be avoided by wiping the necks of the bottles dry after any of the solution has been poured from them; but it will usually be found more convenient to replace the glass stoppers with plugs of vulcanized caoutchouc, or better still, with small glass stoppers, over the bodies of which short pieces of caoutchouc tubing have been stretched. Solutions of the caustic alkalies should be kept in bottles made of glass which is free from lead.

NaHS 23. **Sulphurate of Sodium.** — Dissolve 1 part by weight of commercial sulphide of sodium, if it can be obtained, in 8 parts of water. Sulphide of sodium may be made by melting together in an iron pot or ladle a mixture of dry carbonate of sodium with an equal weight of sulphur. This operation does not require a great deal of heat and it may be performed over the blast lamp or over an ordinary coal fire. Sulphide of potassium is not an available substitute for sulphide of sodium.

Na₂CO₃ 24. **Carbonate of Sodium.** — For most purposes it is essential that the sodium carbonate should be free from sodium sulphate. Pure dry carbonate may be obtained from the dealers in fine chemicals or it may be prepared by washing a pound or two of bicarbonate of sodium repeatedly, upon a filter, with small quantities of ice-cold water, until the original quantity is reduced to a fifth or a sixth of its bulk. The powder is then dried, ignited, and kept in well-stoppered bottles.

25. **Biborate of Sodium.** — Common borax, powdered.

26. **Phosphate of Sodium.** — Dissolve 1 part, by weight, of "common phosphate of soda" in 10 parts of water.

C₂H₃O₂ Na 27. **Acetate of Sodium.** — Dissolve 1 part of the crystallized salt in 10 parts of water.

NaNO₃ 28. **Nitrate of Sodium.** — Select a clean white sample of the commercial salt and keep in the form of a coarse powder.

29. **** Acid Sulphate of Sodium.** — Heat a mixture of 16 parts, by weight, of Glauber's salt, and 5 parts of concentrated sulphuric acid, in a platinum vessel, until a portion of the melted mass becomes distinctly solid when taken up on a glass rod. Then allow the mixture to become cold; remove the cold lump from the platinum vessel, and break it into fragments. Keep the coarse powder in a tight, glass-stoppered bottle.

K₂SO₄ 30. **Sulphate of Potassium.** — Dissolve one part, by weight, of the crystallized salt in 200 parts of water. A solution of this

strength contains the same proportional quantity of sulphuric acid as is contained in a saturated aqueous solution of sulphate of calcium. Hence it cannot precipitate the latter when added to solutions of the soluble calcium salts.

K_2CrO_4 **31. Chromate of Potassium.** — (The normal or "neutral" yellow chromate.) Dissolve 1 part, by weight, of the salt in 8 parts of water.

K_2CrO_7 **32. Dichromate of Potassium.** — The pure crystallized salt is kept in the form of powder. It must be entirely free from chloride.

$K_4FeC_6N_4O_{12}$ **33. Ferrocyanide of Potassium.** — (*Yellow Prussiate of Potash.*) Dissolve 1 part, by weight, of the commercial salt in 12 parts of water.

34. ** Ferricyanide of Potassium. — (*Red Prussiate of Potash.*) Since the aqueous solution of this salt undergoes decomposition, with formation of some ferrocyanide, when kept for any length of time, the salt should be kept for use in the form of powder. The commercial salt is pure enough for analytical purposes. A minute fragment of it may be dissolved in water at the moment of use.

KCN **35. ** Cyanide of Potassium.** — The better sorts of the commercial article are pure enough for analytical purposes. It should be kept in the solid form in a tightly stoppered bottle. When the solution is required, dissolve 1 part of the salt in 4 parts of cold water.

KNO_3 **36. Nitrate of Potassium.** — Refined saltpetre may be employed. It should be kept in the state of powder.

KNO_2 **37. ** Nitrite of Potassium.** — Weigh out 8 parts of concentrated nitric acid, mix it with an equal weight of water, and place the mixture in a glass flask provided with a perforated cork and gas delivery-tube. The flask should be so large that the mixture only half fills it. Throw into the liquid 2 parts of starch, in lumps, and heat the mixture until red fumes of nitrous and hyponitric acids begin to be given off; then remove the lamp lest the action become too violent. Conduct the fumes into a bottle containing 5 parts of potash-lye of 1.27 sp. gr., until the latter is saturated. Then filter the saturated liquid, and evaporate it to dryness. For use, dissolve 1 part of the dry salt in 2 parts of water.

The nitrite of potassium bought of dealers in fine chemicals is often unfit for the uses prescribed in this manual; it can readily be

made good, however, by dissolving it in twice its weight of water and saturating the solution with nitrous fumes.

KI 38. *Iodide of Potassium and Starch Papers. — Dissolve a gramme of pure iodide of potassium (free from iodate) in 200 cubic centimetres of water. Heat the solution moderately in a porcelain dish, and stir into it ten grammes of starch which has been reduced to the consistence of cream by rubbing it in a mortar with a small quantity of water. Stir the mixture until it gelatinizes, taking care not to burn the starch, then allow the paste to cool, and spread it thinly upon one side of white glazed paper with a wooden spatula. Dry the paper, cut it into strips as large as the little finger and preserve it in stoppered bottles kept carefully closed.

AgNO₃ 39. Nitrate of Silver. — Dissolve 1 part, by weight, of the commercial crystals in 20 parts of water.

40. *Slaked Lime. — Mix common quicklime with half its weight of water. Keep the powder in bottles with tight stoppers.

41. *Lime Water. — Place a handful of slaked lime in a large bottle, pour in enough water to almost fill the bottle, cork the latter tightly, and shake it at intervals during several days. Decant the clear liquid into smaller bottles for use. Refill the large supply-bottle with water, and again shake it at intervals.

CaCl₂ 42. Chloride of Calcium. — Stir powdered white marble into dilute chlorhydric acid until the acid is saturated, and dilute 1 part of the concentrated solution with 5 parts of water.

BaCl₂ 43. Chloride of Barium. — Dissolve 1 part, by weight, of the commercial salt in 10 parts of water.

Ba(NO₃)₂ 44. **Nitrate of Barium. — Dissolve 1 part, by weight, of the commercial salt in 15 parts of water.

(C₂H₃O₂)₂Pb 45. Acetate of Lead. — Dissolve 1 part, by weight, of "sugar of lead" in 10 parts of water.

46. *Lead Paper. — Wet strips of white paper in a solution of acetate of lead, or better, in a solution of subacetate of lead, and dry them in air which is free from sulphuretted hydrogen. Cut the dried paper into slips as large as the little finger, and keep the slips in tightly stoppered bottles. Or, paper may be slightly moistened with a solution of acetate of lead at the moment of use.

47. Sulphate of Magnesium and Chloride of Ammonium. — Dissolve 24.6 grammes of Epsom salt and 33 grammes of commercial chloride of ammonium in water, add some ammonia-water to the solution and dilute the liquor to the volume of a litre.

If less than a litre of the reagent is required, the weights above given may, of course, be reduced in any desired proportion. Filter the solution to separate any precipitate of ferric hydrate or other insoluble matters, which may have been present as impurities in the components of the mixture, and preserve the clear liquid.

From a solution thus prepared no hydrate of magnesium can be precipitated by ammonia-water; herein consists the advantage of the mixture as a test for phosphoric and arsenic acids.

Fe_2Cl_6 48. **** Ferric Chloride.** — This solution is prepared by passing chlorine gas through a saturated solution of iron tacks in chlorhydric acid, until a drop of the fluid no longer produces a blue precipitate in a solution of ferricyanide of potassium. The solution is then heated to expel the excess of chlorine.

$Co_2NO_3.6H_2O$ 49. **** Nitrate of Cobalt.** — Dissolve 1 part, by weight, of the crystallized salt in 10 parts of water.

$CuSO_4$ 50. **** Sulphate of Copper.** — Dissolve 1 part, by weight, of the crystallized salt (blue vitriol) in 10 parts of water.

51. **** Protochloride of Tin.** — This solution is prepared by boiling scraps of tin with strong chlorhydric acid until hydrogen ceases to be evolved. The tin must be in excess. The solution is diluted with four times its bulk of water acidulated with chlorhydric acid, and filtered, if necessary. The clear liquid must be kept in a tightly closed bottle containing some bits of tin.

MnO_2 52. **** Black Oxide of Manganese.** — The artificially prepared pure binoxide of manganese.

HgO 53. **** Red Oxide of Mercury.** — The commercial oxide. It should leave no residue when heated upon platinum foil.

$HgCl_2$ 54. **** Chloride of Mercury.** — Dissolve 1 part of "corrosive sublimate" in 16 parts of water.

$PtCl_2$ 55. **** Bichloride of Platinum.** — Cut a small quantity of worn-out platinum foil into very fine pieces and boil them in a porcelain dish, with successive small portions of aqua regia until all the metal has been dissolved. Collect the several portions of aqua regia, partially saturated with platinum, in another dish, and evaporate the liquid to dryness on a water bath. Dissolve the residue in 10 parts of water for use.

Zn 56. **Zinc.** — The commercial sheet metal, although usually contaminated with lead and cadmium and often containing faint traces of arsenic and sulphur, will generally be found pure enough for the purposes of this manual.

57. **“Solution of Indigo” (Sulphindigotic Acid).— Pour 5 parts (5 grammes will be ample) of fuming sulphuric acid into a beaker, place the latter in a dish of water to keep it cool, and stir into the acid, little by little, 1 part of finely powdered indigo. When all the indigo has been added to the acid, leave the mixture at rest for 48 hours; then pour it into 20 times its own volume of water, filter the mixture and preserve the filtrate for use. Instead of 6 parts of fuming sulphuric acid, 12 or 14 parts of the ordinary strong acid may be employed; in this case, however, the mixture must be heated for several hours on a water-bath.

58. Litmus Paper.— Heat 1 part, by weight, of commercial litmus with 6 parts of water, upon a water bath for several hours, taking care to replace the water which evaporates. Filter, divide the filtrate into two equal portions, and stir one half repeatedly with a glass rod dipped in very dilute nitric acid, until the color appears distinctly red. Pour the blue and red halves into a porcelain dish, and stir the mixture. Draw strips of fine unsized paper through the liquid, and hang them on cords to dry. The color of the paper thus obtained is not blue but bluish-violet. It turns blue when touched with an alkali, and red when exposed to acids, and may be used indifferently as a test for either acids or alkalies.

59. Starch Paste should be prepared, when wanted for use, by boiling 80 cubic centimetres of water in a porcelain dish, and stirring into it half a gramme of starch which has previously been reduced to the consistence of cream by rubbing it in a mortar with a few drops of water.

60. * Alcohol.— Common alcohol of 85 or 90 per cent.

61. Water.— Clean rain water will serve well enough for most of the purposes of this manual. In granitic regions the water of many lakes, brooks and ponds also is nearly pure. Pure water may be obtained by melting blocks of compact ice, or by distilling ordinary water in glass or copper retorts and rejecting the first portions of the distillate. It should yield no precipitate when tested with chloride of barium and nitrate of silver.

61a. Hypochlorite of Sodium.— The “chloride of soda” of the druggists.

C_2H_6O
 H_2O

$NaClO$

SOLUTIONS OF KNOWN COMPOSITION.

62. In case the experiments indicated in Part I are to be performed by a considerable number of students, it will be found convenient to prepare beforehand a moderate supply of the various solutions required in making the known mixtures under the several classes. These solutions may be made of the strengths indicated below.

Chloride of Copper. — Dissolve black oxide of copper in 5 times its weight of a mixture of equal parts of strong chlorhydric acid and water. Dilute the resulting solution with 3 times its bulk of water. [A single student in performing the experiment, may dissolve a few grains of the oxide in a small quantity of the strong acid, and, in general, may make the solutions as needed for use by taking a crystal or a small amount of the required substance in powder, as the case may be, without regard to the exact amount. It is well, however, not to start with such quantities as to make the precipitates inconveniently bulky.]

Arsenious Acid. — Dilute a quantity of chlorhydric acid with half its bulk of water and saturate it with arsenious acid at a gentle heat. When the solution has become cold, pour off the clear liquor from the arsenious acid which has crystallized out.

Ferrous Chloride. — Treat warm dilute chlorhydric acid (App., § 3) with as much iron (wire or filings) as it will dissolve and then dilute the solution with an equal bulk of water. [This solution should be prepared only in small quantity and kept in a well-stoppered bottle.]

Chloride of Zinc. — To a quantity of chlorhydric acid diluted with an equal bulk of water, add as much zinc as the acid will dissolve and then add to the solution 5 times its bulk of water.

Chloride of Calcium. — Stir powdered white marble or chalk into chlorhydric acid diluted with twice its bulk of water until the acid is saturated; filter the solution if necessary.

Chloride of Magnesium. — Add "magnesia alba" to dilute chlorhydric acid until the acid is saturated, then dilute the solution with twice its bulk of water.

Chloride of Sodium. — Dissolve common salt in 10 times its weight of water.

Nitrate of Silver. — Dissolve the crystallized salt in 10 times its weight of water.

Mercurous Nitrate. — Dilute a small quantity of strong nitric acid with an equal bulk of water, and to the mixture, warmed over the lamp, add more mercury than will dissolve. When action has ceased dilute the solution with 5 times its bulk of water and keep in a bottle containing a small amount of metallic mercury.

Nitrate of Lead. — Dissolve the crystallized salt in 5 times its weight of water.

Mercuric Chloride. — Dissolve corrosive sublimate in 20 times its weight of water.

Chloride of Bismuth. — Dissolve metallic bismuth in aqua regia. When the acid is saturated pour off the solution from the undissolved metal, dilute it with twice its bulk of water and add strong chlorhydric acid to dissolve the precipitated oxy-chloride. Or, dissolve the commercial sub-nitrate in chlorhydric acid and dilute as before.

Chloride of Cadmium. — Dissolve the commercial salt in 10 times its weight of water.

Chloride of Lead. — Boil dilute chlorhydric acid with an excess of litharge and filter the solution when perfectly cold.

Chloride of Antimony. — Dilute the commercial strong solution with an equal bulk of water and add strong chlorhydric acid to dissolve the basic chloride which is precipitated. Or, dissolve the finely powdered metal in aqua regia and dilute as before.

Sulphate of Manganese. — Dissolve the crystallized salt in 10 times its weight of water.

Common Alum. — Dissolve in 10 times its weight of water.

Chrome Alum — Dissolve in 10 times its weight of water.

Bone Ash (p. 38) had better be kept in powder and dissolved as needed, in order that the student may not lose sight of the fact that this compound requires an acid solvent:

Nitrate of Cobalt. — Dissolve in 10 times its weight of water.

Nitrate of Nickel. — Dissolve in 10 times its weight of water. (The chlorides of nickel and cobalt answer equally well and the solutions may be made of the same strength.)

Chloride of Barium. — Dissolve the crystallized salt in 5 times its weight of water.

Chloride of Strontium. — Dissolve the crystallized salt in 5 times its weight of water. (The nitrate will answer equally well.)

Nitrate of Potassium. — Dissolve 1 part of the commercial salt in 5 parts of water.

Sulphate of Sodium. — Dissolve 1 part of Glauber's salt in 10 parts of water.

Phosphate of Sodium. — Dissolve commercial "phosphate of soda" in 10 parts of water as in App., § 26.

Carbonate of Sodium. — Dissolve 1 part of "sal soda" in 5 parts of water.

Oxalate of Potassium. — Dissolve 1 part of the crystallized salt in 5 parts of water.

Tartrate of Potassium. — Dissolve tartaric acid in 5 times its weight of water and neutralize it exactly with carbonate of potassium.

Iodide of Potassium. — Dissolve 1 part of the crystallized salt in 10 parts of water.

UTENSILS.

63. The implements required by the student of qualitative analysis are few and simple. Besides bottles for the reagents enumerated in the foregoing list, and a few small phials for the preservation of samples of salts and mixtures to be analyzed, there will be needed:—

A dozen test-tubes,	A wash-bottle,
A wooden test-tube rack,	2 small evaporating dishes,
A test-tube brush,	A porcelain crucible,
A nest of small beakers,	1 triangle of iron-wire,
2 or 3 glass stirring-rods,	An iron ring-stand,
A small thistle-, or funnel-tube,	A filter-stand,
A larger thistle-tube for the gas-generator,	A lamp,
1 stick of No. 7 glass tubing (see App., § 82),	A gas-bottle for generating sulphuretted hydrogen,
2 or 3 sticks of No. 4 glass tubing,	A common jeweller's blowpipe,
3 small glass funnels,	A pair of small iron pincers (jeweller's tweezers),
A small glass flask,	A piece of platinum foil,
	A bit of platinum wire,

A small platinum crucible is also very desirable,	A few corks or caoutchouc stoppers,
A few packages of cut filters, or a quire of filter paper,	A piece of blue cobalt glass (see § 42).

64. Reagent Bottles.—The bottles in which reagents are kept should be of cylindrical shape, and rather high than wide. They should be closed with glass stoppers which fit accurately, but are not very finely ground. The stoppers should have upright (not mushroom-shaped) heads. Most of the liquid reagents may be conveniently kept in narrow-mouthed bottles of the capacity of 6 fluid ounces; but to avoid the necessity of frequently refilling the bottles, it is well to keep the solutions most commonly employed—namely, dilute chlorhydric and nitric acids, ammonia-water, chloride of ammonium and carbonate of ammonium—in 8-ounce bottles. Care must be taken in this case to choose bottles of such shape that they can be readily grasped between the thumb and fingers.

For the reagents which are to be kept in the dry state, wide-mouthed bottles of the capacity of 2 or 3 ounces should be chosen.

Reagent bottles should always be made “extra-heavy,” since, from constant use, they are exposed to many blows. The lustrous “flint-glass” bottles of American or English make are ill suited for the preservation of liquid reagents; for such glass is easily attacked by many chemical agents, and is therefore likely to render the reagents impure. German bottles are usually to be preferred. They are made of glass free from lead, have round shoulders and well-ground stoppers, and are often numbered both upon the bottle and the stoppers, so that the proper place of the latter can always be discovered. French bottles, though made of good glass and sold at a low price, have often such square shoulders that it is wellnigh impossible to empty them completely, and often difficult to pour out a liquid from them drop by drop. Their stoppers, moreover, are usually too finely ground, and are hence constantly liable to stick fast.

Each reagent bottle should be kept in a particular place on shelves before the operator and convenient to his hand. Whenever a reagent is to be used, the bottle which contains it should be grasped in the right hand; the stopper should be taken out by pinching it between the first and second or third and fourth fingers of the left hand, or by pressing it between the little finger and palm of that hand. In either case, the bottle is withdrawn from the stopper, and not the stopper from the bottle. Neither bottle nor stopper should be put upon the table; the stopper should be held in the left hand

as long as the bottle is open. When the reagent has been poured out, the bottle is immediately closed, and returned to its place upon the shelf. If these apparently trifling particulars are scrupulously attended to, no stopper can ever be misplaced, or soiled by contact with liquids or dirt on the table; and the bottle will always be found in its proper place when instinctively reached for. Moreover, the label on the bottle cannot be injured by drops of the reagent, since the liquid must necessarily be poured from the back, or blank side of the bottle.

When a stopper sticks tightly in the neck of a bottle, it may sometimes be loosened by pressing it first upon one side, and then upon the other, with the thumb of the right hand, while the fingers of that hand grip the bottle, and the bottle is held still with the left hand. Or the neck of the bottle may be immersed in hot water for a minute or two, to expand the glass outside the stopper. The stopper can then usually be taken out without trouble. The hot water may be conveniently applied by pouring a slow stream of it from a wash-bottle upon the neck of the bottle. Another way is to heat the neck of the bottle over a very small flame of the gas or alcohol lamp. No matter how the glass is heated, the bottle must be constantly turned round and round, in order that each side of the neck may be equally exposed to the heat and the risk of cracking the bottle so be lessened.

65. Test-tubes are little cylinders of thin glass with round thin bottoms and lips slightly flared. Their length may be from five to seven inches, and their diameter from one half to three fourths of an inch; they should never be so wide that the open end cannot be closed by the ball of the thumb.

Test-tubes are used for heating small quantities of liquid over the gas- or spirit-lamp; they may generally be held by the upper end in the fingers without inconvenience; but in case they become too hot to be held in this way, a strip of thick folded paper may be nipped round the tube, and grasped between the thumb and forefinger just outside the tube.

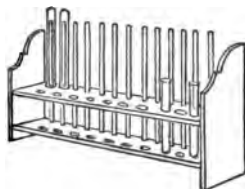
Two precautions are invariably to be observed in heating test-tubes: — 1st. The outside of the tube must be wiped perfectly dry; and 2d. The tube must be moved in and out of the flame for a minute or two when first heated. It should be rolled to and fro also to a slight extent between the thumb and forefinger, in order that each side of it may be equally exposed to the flame. A drop of water on the outside of the tube keeps one spot cooler than the rest. The tube breaks, because its part, being unequally heated, expand unequally, and tear apart.

When a liquid is boiling actively in a test-tube, it sometimes happens that portions of the hot liquid are projected out of the tube with some force; the tube should therefore always be held in an inclined position, and the operator should be careful not to direct it towards himself, or towards any other person in his neighborhood.

Test-tubes are cleaned by the aid of cylindrical brushes made of bristles caught between twisted wires, like those used for cleaning lamp-chimneys; the brushes should have a round end of bristles.

66. Test-tube Rack. — Test-tubes are kept in a wooden rack, such as is represented in Figure 1. When in use, the tubes stand upright in the holes of the rack; but clean tubes are inverted upon the pegs behind the holes, in order that they may be kept free from dust, and that the last portions of wash-water may drain away from them after washing. The rack should be large enough to hold a dozen tubes. Care should be taken that the tubes are washed perfectly clean before being inverted on to the pegs lest the pegs themselves become dirty.

Fig. 1.



67. Flasks. — Small Berlin flasks of two or three ounces capacity are well suited for the purposes of qualitative analysis. These German flasks are tough, capable of withstanding sudden changes of temperature, and durable, although their bottoms and sides have all the requisite thinness. When a liquid is to be boiled in a flask, the flask should be placed upon a support of wire-gauze (App., § 76), and sufficiently inclined to prevent any particles of the liquid from being thrown out of the neck by the movement of ebullition.

As with test-tubes and all other glass or porcelain vessels of whatever form, the outside of a flask must be wiped perfectly dry before exposing it to the lamp. The flame should be moved about also beneath the flask, at first, in order that the temperature of the latter may be raised equally and not too rapidly.

68. Beakers are thin, flat-bottomed tumblers with a slightly flaring rim. They are bought in sets or nests. A nest in which the largest sized beaker has a capacity of about 6 ounces will be sufficient for the requirements of this work.

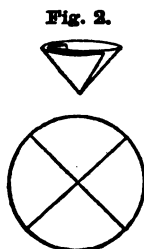
69. Glass Funnels should be thin and light, and should be about 2 or 2.5 inches in diameter. Their sides should incline at an angle of 60°. The wider the throat of the funnel the better.

70. Filtering. — Paper filters are employed in qualitative analy-

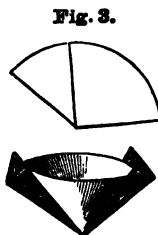
sis to separate precipitates from the liquids in which they have been formed. A good filtering-paper must be porous enough to filter rapidly, and yet sufficiently close in texture to retain the finest powders; and it must also be strong enough to bear, when wet, the pressure of the liquid which is poured into upon it. Filter-paper should never contain any gypsum or other soluble material, and should leave only a small proportion of ash when burned. White or light-gray paper is to be preferred to colored, since it more commonly fulfils these requirements.

Filtering-paper is commonly sold in sheets, which may be cut into circles of any desired diameters for use, according to the various scales of operation, and quantities of liquids to be filtered. Or packages of "cut-filters" may be procured ready-made from the dealers in chemical wares.

As a general rule, small filters should be employed in analytical operations; the mixture to be filtered should be poured by small successive portions upon a filter no larger than is needed to hold the whole of the solid matter which is to be collected. Filters about three inches in diameter are well suited for most of the analytical operations described in this work, though there are many cases where smaller filters are required, and a few instances in which filters as large as four inches in diameter might be necessary.



There are two ready methods of preparing filters for use. According to the first method, shown in Fig. 2, a circle of paper is folded over on its own diameter, and the semicircle thus obtained is folded once upon itself into the form of a quadrant; the paper thus folded is opened so that three thicknesses shall come upon one side, and one thickness upon the other, as shown in the upper half of Fig. 2; the filter is then placed in a glass funnel, the angle of which should be precisely that of the opened paper, viz., 60° . The paper may be so folded as to fit a funnel whose angle is more or less than 60° , but this is the most advantageous angle, and funnels should be selected with reference to their correctness in this respect.



In the second method of folding filters, the circle of paper is doubled once upon itself as before into the form of a semicircle, and a fold equal to one quarter of this semicircle is turned down on each side of the paper. Each of the quarter semicircles is then folded back upon itself, as shown in the lower half of Fig. 3;

the filter is opened, without disturbing the folded portions, and placed in the funnel. Filtration can be rapidly effected with this kind of filters, for the projecting folds keep open passages between the filter and the funnel, and thus facilitate the passage of the liquid. That portion of the circle of paper, which must necessarily be folded up in order to give the requisite conical form to a paper filter, retards filtration in the first manner of folding, but helps it in the second.

A filter should always be moistened with water after it has been placed in the funnel, in order that the fibres of the paper may be swollen and the size of its pores diminished, before any of the matter to be filtered can pass into them.

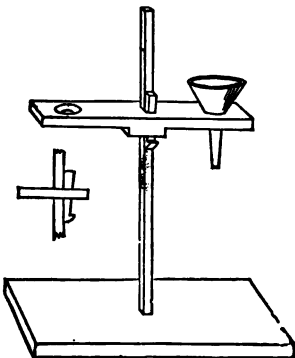
Coarse and rapid filtration—as in the preparation of reagents—can be effected with paper filters of large size, or with cloth bags; also by plugging the neck of a funnel or leg of a siphon loosely with tow or cotton. If a very acid or very caustic liquid, which would destroy paper, cotton, tow or wool, is to be filtered, the best substances wherewith to plug the neck of the funnel are asbestos and gun-cotton, neither of which is attacked by such corrosive liquids.

Fig. 4.



71. Filter-Stand.—Filters less than two inches in diameter may be placed directly in the mouth of a test-tube without need of even a funnel to support them; and in general the funnel which holds a filter may be thrust directly into the mouth of a test-tube whenever the quantity of liquid to be filtered is small, if only an ample exit be provided for the air in the tube, in the manner shown with the bottle of Fig. 4.

Fig. 5.



But when the quantity of liquid to be filtered is comparatively large, or the operations to which the filtrate is to be subjected require that it should be collected in a beaker or porcelain dish, the funnel should have an independent support. The iron ring stand, described in § 76 of this Appendix, may be used for this purpose in case of need; but wooden stands of the form represented in Fig. 5, adapted expressly for holding funnels, are very

convenient and not expensive. The horizontal bar which holds the funnel may be fixed at any height on the vertical square rod by means of a wedge-shaped key, whose form is shown in the figure. A fine-grained wood, which does not swell or shrink much, is desirable for filter-stands.

In general, care should be taken that the lower end of the funnel touch the side or edge of the vessel into which the filtrate descends, in order that the liquid may not fall in drops, but run quietly without splashing.

72. Rapid Filtration.—Since in the course of an analysis much time is consumed in the process of filtration, it is desirable that this operation should be made as rapid as possible. A considerable advantage over the ordinary method may be gained by increasing the length of the tube of the funnel by the addition of a

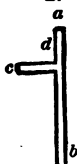
Fig. 6.



piece of glass-tubing a metre or so in length and bent as represented in Fig. 6. When the funnel and the tube are filled with liquid, the difference of pressure on the upper and lower surfaces is great enough to cause a very sensible increase in the rapidity of the filtration. A far more efficient method of hastening the process of filtration by causing a difference in pressure on the upper and lower surfaces of the liquid to be filtered, may be made available wherever a constant supply of water with a fall of 8 or 10 feet can be obtained. The details of the process and of a convenient form of the apparatus which may be employed, will be described presently; the principle of the method is as follows:—

The filtrate instead of being received in a beaker as is usual, is received in a flask from which the air is more or less completely exhausted. This exhaustion is accomplished by the use of a sort of "water-pump" which is an adaptation of a very simple principle. Let $a b$ and $c d$ be two tubes, arranged as represented in Fig. 7. If water be allowed to flow in a constant stream down the tube $a b$ and the amount of water supplied be properly regulated, that part of the tube $a b$ which is below the junction with $c d$ will be filled with bubbles of air, which is drawn in continuously through $c d$ and dragged down by the falling water;

Fig. 7.



if the tube at c be connected with a closed vessel, the air in the vessel will be gradually exhausted. The efficiency of such a pump depends in a measure upon the relative size of the tubes and the

amount of water supplied. Various forms of apparatus in which advantage is taken of this general principle might be and have been devised. As adapted for purposes of filtration the apparatus is known as Bunsen's "filter-pump"; on account of the great advantage to be gained by its use, the apparatus, and the method of conducting the filtration will be given in detail.

A strong glass flask (for the purposes of qualitative analysis, one of from 2 to 4 ounces capacity will answer) is furnished with a doubly-perforated caoutchouc stopper: through one of the perforations is thrust the neck of a glass funnel and through the other a piece of No. 7 glass tubing, bent at a right angle.

This tube serves to connect the flask with the apparatus designed to effect the rarefaction of the air in the flask. If any considerable difference of pressure were brought about between the upper and lower surfaces of the liquid in the funnel, the filter would most likely break and allow the precipitate to fall into the flask. This danger is obviated as follows:

— A funnel is chosen possessing an angle as near 60° as possible, the walls of which must be free from inequalities of every sort. Into this glass funnel is fitted a second funnel or rather cone of thin platinum foil, the sides of which possess exactly the same inclination as those of the glass funnel. This platinum cone is made by cutting out from a piece of the thinnest platinum foil that can be obtained, a portion of a circle as represented in Fig. 9, *a*. For use with a funnel two inches in diameter, this circle may conveniently have a radius of 1 inch. The foil is then laid upon a piece of

hard wood and a number of small holes are punched out of it. A ready implement for this purpose may be made by grinding off squarely the point of a common sewing-needle and fitting the needle to a wooden handle. When gently tapped with a hammer, this punch forces out a small round bit of the foil and, by subsequently rubbing the foil on the bottom of a mortar with the pestle, any inequalities of surface are avoided. When the foil has been annealed by being heated to redness in the lamp and allowed to cool, it is bent up into the shape of a cone as represented in Fig. 9, *b*. This cone should have the same angle of inclination as the funnel in which it is to be used, and it is desirable that the funnel should be of an angle of 60° ; still if the funnel be *regular* in shape, it can be used although it varies somewhat from this angle. The cone is best fitted to the funnel by the following manipulation.

Fig. 8.

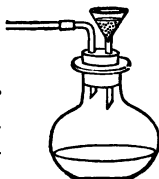
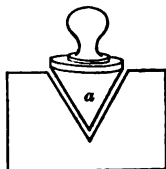


Fig. 9.



A solid cone of close-grained hard wood, or better of brass (Fig. 10, *a*), which has been turned to an angle of 60° , is laid upon the platinum foil in such a position that the apex of the cone comes at the centre of the circle of which the foil forms a part; the foil is then folded up and shaped with the fingers so that it fits the cone closely. The two edges of the foil lap, and if they were soldered in this position the cone would, of course, have an angle of 60° . The platinum cone is now inserted in the funnel to be used, and opened out a little with the fingers, if necessary, so that it fits

Fig. 10.

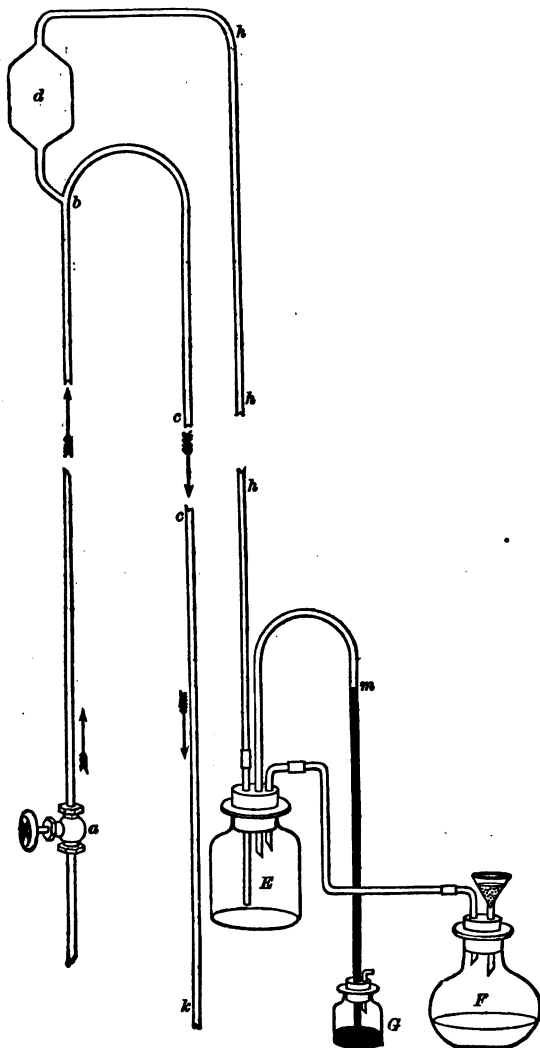


the glass. The funnel should differ so little from 60° that the edges overlap each other only slightly more or slightly less than when the foil was fitted to the wooden cone.* By means of a sharp point make two scratches on the platinum cone, to show where the overlapping edges come when the foil is in position, and then remove the cone from the funnel. Hold the platinum by means of a pair of pincers in the same position that it occupied when in the funnel, which is easily done by observing the scratches made. Then heat the cone (Fig. 9, *b*) at the outer overlapping edge, with a blow-pipe flame, put on a small amount of powdered borax, heat again, then put on a bit of pure gold and heat until the gold melts and solders the two edges together. The cone should be held, the gold put on, and the blowpipe-flame directed in such a manner that the melted gold will run down towards the apex of the cone and not in the contrary direction. After dissolving off the adhering borax with warm water, the cone is ready for use. An ordinary paper filter, folded according to the first method of App., § 70 is introduced into this compound funnel in the usual manner; when carefully moistened and so adjusted that no air-bubbles are visible between it and the glass, this filter, when filled with a liquid, will support the pressure even of an extra atmosphere without breaking.

A convenient form of the Bunsen pump is represented in Fig. 11. The tubes (*ab*, *bc*, *hh*) which are represented in the figure may be very conveniently made of quarter-inch lead pipe (see also, p. xxii, near bottom) and the bulb-like enlargement at *d* may also be made of

* This wooden or brass cone is not essential; the platinum cone could be shaped in the funnel with proper care; it is, however, very convenient, especially in a laboratory where there are a number of students. In procuring such a cone, it is well to lay out with a protractor on a piece of thin sheet tin an angle of 60° , cut this out and then to give the pattern (templet) to the workman employed.

Fig. 11.



of lead and soldered on to the smaller pipe. The water is supplied in *not too large amount* by the cock *a*, and as it passes along the pipe *a b c* and into the waste *c k*, it carries with it a continual stream of air bubbles dragged through *h d*. This tube, *h d*, communicates indirectly with the flask *F* which is not connected immediately with the pump; the connection is interrupted by the bottle *E*, furnished with a perforated stopper through which pass three glass tubes. One of these tubes connects with the flask *F*; one (by means of caoutchouc tubing) with the lead pipe *h*; one with the manometer *m*. The object of this bottle *E* is to prevent the flow of water into the flask *F*, in case, as sometimes happens, the operator in letting on too rapid a stream of water causes it to rise in the bulb *d* and flow over into the tube *h h*. All the connectors should be of very thick caoutchouc tubing tightly fitted and then varnished with a strong solution of shellac; the stopper of the bottle *E* may be treated in the same manner.

The manometer-bottle *G* is a convenient but not absolutely essential addition. It consists simply of a small bottle containing a quantity of mercury, to the surface of which the atmosphere has access through a small glass tube. The tube *m* dips below the mercury and connects with the bottle *E*. As the air is rarified in *E* (and in the flask *F*), the mercury rises in the tube *m*; this tube may be divided into centimetres or inches by means of a file, or it may be provided with, or attached to, a paper or wooden scale.

The amount of rarefaction that can be produced by this means depends, of course, upon the head of water accessible, and this will be determined by the difference in height between the points *b* and *k*, the extremity of the waste-pipe. With a fall of 35 ft. it is possible to obtain nearly a perfect vacuum, but a fall of 8 or 10 feet is sufficient for the purposes of qualitative analysis.

In operating the filter-pump certain precautions should be observed. Care should be taken that the water be not supplied in too large an amount. To this end it is well to have the cock or valve so arranged as to make it impossible to let on more water than experience shows to be necessary. The greatest effect is produced by the smallest amount of water that will drag the air down the pipe *c k* in the form of bubbles, and in order to observe the flow of air it is well to make a portion of the pipe *k* of glass. (For that matter, all the pipes may be made of glass tubes joined by thick caoutchouc connector; glass tubing of size No. 5 (see App., § 82) will answer; and the bulb *d* may also be blown of glass by a person possessing sufficient skill.) In using the pump the water should be let on before

the connection is made with the filtering flask and the flask should be removed before the water is shut off.*

73. Porcelain Dishes and Crucibles. — Small open dishes which will bear heat without cracking, are much used for boiling and evaporating liquids. The best evaporating-dishes are those made of Berlin porcelain, glazed both inside and out, and provided with a little lip projecting beyond the rim. The dishes made of Meissen porcelain are not glazed on the outside, and are not so durable as those of Berlin manufacture; but they are much cheaper, and with proper care last a long time.

The small Berlin dishes, Nos. "00," "0," and "1," are well suited for all the requirements of this work. They will generally bear an evaporation to dryness and subsequent ignition over the open flame of a gas lamp, — as when ammonium salts are expelled from Class VII (§ 41), — but it is well to protect the dish somewhat by placing it upon a piece of wire-gauze, rather than to support it upon a simple triangle. The Meissen dishes do not so well endure an open flame. The cheaper kinds of evaporating dishes, made of "semi-porcelain," should never be subjected to this severe treatment; they are, for that matter, unfit for use in qualitative analysis.

Very thin, highly glazed porcelain crucibles, with glazed covers, are made both at Berlin, and at Meissen near Dresden. In general the Meissen crucibles are thinner than the Berlin, but the Berlin crucibles are somewhat less liable to crack; both kinds are glazed inside and out, except on the outside of the bottom. The Berlin Nos. "00" and "0," respectively 1 1-4 and 1 1-2 inches in diameter, are best suited for the purposes of this manual. As the covers are much less liable to be broken than the crucibles, it is advantageous to buy more crucibles than covers, whenever it is possible so to do. Porcelain crucibles are supported over the lamp on an iron-wire triangle; they must always be gradually heated, and never brought suddenly into contact with any cold substance while they are hot.

74. Lamps. — The common spirit-lamp will be understood without description from the figure (Fig. 12). When not actually lighted, the wick must be kept covered with the glass cap; for if the wick were exposed to the air, the alcohol in the spirit upon it would evaporate faster than the water, and the cotton would soon become water-soaked and incapable of being lighted.

Whenever gas can be obtained, gas-lamps are greatly to be preferred to the best spirit-lamps. For all ordinary uses, the gas-lamp known as Bunsen's

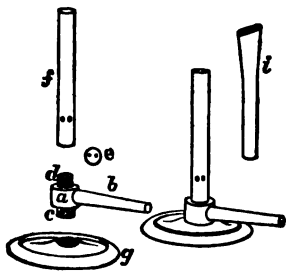
Fig. 12.



* See Note on page xlvi.

burner may be employed. The cheapest and best construction of the lamp may be learned from the following description with the

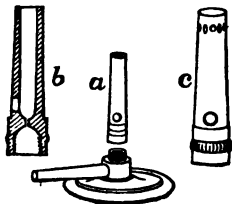
Fig. 13.



accompanying figure. (Fig. 13.) The single casting of brass *a b* comprises the tube *b* through which the gas enters, and the block *a* from which the gas escapes by two or three fine vertical holes passing through the screw *d* and issuing from the upper face of *d*, as shown at *e*. The length of the tube *b* is 4.5 c. m., and its outside diameter varies from 0.5 c. m. at the outer end to 1 c. m. at the junction with the block *a*. The outside diameter of the

block *a* is 1.6 c. m., and its outside height without the screws is 1.8 c. m. By the screw *c*, the piece *a b* is attached to the iron foot *g*, which may be 6 c. m. in diameter. By the screw *d*, the brass tube *f* is attached to the casting *a b*. The diameter of the face *e*, and therefore the internal diameter of the tube *f* should be 8 m. m. The length of the tube *f* is 9 c. m. Through the wall of this tube, four holes 5 m. m. in diameter, are to be cut at such a height that the bottom of each hole will come 1 m. m. above the face *e* when the tube is screwed upon *a b*. These holes are of course opposite each other in pairs. The finished lamp is also shown in the figure. To the tube *b* a caoutchouc tube of 5 to 7 m. m. internal diameter is attached; this flexible tube should be about 1 m. long, and its other extremity should be connected with the gas-cock through the intervention of a short piece of brass gas-pipe screwed into the cock. In cases where a very small flame is required, as, for instance, in evaporating small quantities of liquid, a piece of wire gauze somewhat larger than the opening of the tube *f* should be laid across the top of the tube, and its projecting edges pressed down tightly against the sides of the tube before the gas is lighted. In default of this precaution, the flame of a Bunsen burner, when small and exposed to currents of air, is liable to pass down the tube and ignite the gas at *d*.

Fig. 14.



A smaller and somewhat cheaper lamp, made on the same principle as the ordinary Bunsen burner, is represented in Fig. 14. The "tip" of the burner is cast of brass, and the construction will be evident from the enlarged section (*b*). The stand or foot

is the same as shown in Fig. 13, except that the opening for the gas is larger. These lamps are excellent where a small flame is required, as it is almost impossible for the gas to "back down" and ignite at the lower opening. Tips are also made, as shown at *c*: here the upper opening is closed, and the gas issues from smaller openings in the sides of the tube forming a "rose"; this form of burner is of especial service when evaporating a solution in a porcelain dish where it is desirable to heat the liquid equably. Either of the tips described may be screwed upon an ordinary gas-burner in default of the stand or foot above represented. These burners can be procured of M. W. Pierce & Co., Gas and Steam Fitters, Boston, Mass.

75. Blast-lamps and Blowers. — Though well suited for all the ordinary operations of the laboratory, the lamps above described are incapable of yielding a very intense heat. Hence, when the contents of a platinum crucible are to be fused or intensely heated, a blast-lamp will be found useful. The best form is that sold under the name of Bunsen's Gas Blowpipe. Its construction and the method of using it may be learned from the accompanying figure; *a b* is the pipe through which the gas enters, *c* is the tube for the blast of air; the relation of the air-tube to the external gas tube is shown at *d*; there is an outer sliding tube by which the form and volume of the flame can be regulated.

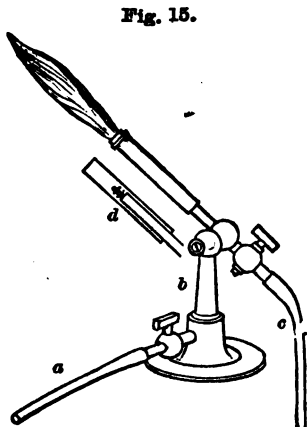


Fig. 15.

If gas is not to be had, a lamp burning oil or naphtha may be employed. Figure 16 represents a glass-blower's lamp, made of tin and suitable for burning oil. A large wick is essential, whether oil or naphtha be the combustible.

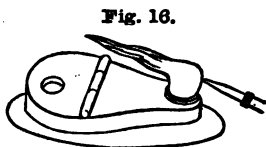
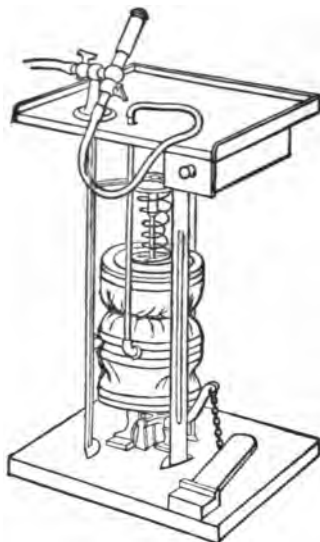


Fig. 16.

For every blast-lamp a blowing-machine of some sort is necessary. To supply a constant blast it is essential that the bellows be of that construction called double.

Fig. 17 represents a very good form of blowpipe-table, made by J. H. Call, North Billerica, Mass., and costing about thirty dollars. The bellows are made of seamless rubber cloth; the table is 0.8 metre

Fig. 17.



high, from which the other dimensions may be inferred. A simple form of bellows, and one which can be made by any carpenter or cabinet-maker, is represented in perspective and in section in

Fig. 18.



Fig. 18. The sides of the bellows and of the reservoir are made of stout leather. The arrangement of valves will be evident from the figure; a constant pressure is maintained on the reservoir by means of a spiral spring, and the air is delivered through the tube *t*. The rod which is represented in the figure serves simply as a guide. The entire length from *a* to *b* may be 0.6 metre.

Where an abundant supply of water is at command, a Bunsen pump of the kind described in App., § 72, but of larger size, may be used to furnish a blast. The pipe above the enlargement *d* (see Fig 11) is left open to the air instead of connecting with a flask as represented in Fig. 11. The waste-pipe *k* passes through the cork of large bottle, Fig. 19, of some litres capacity. Through the stopper of this bottle there pass also two glass tubes; one of them, *h*, reaches nearly to the bottom of the bottle and serves as a siphon; the other merely extends through the cork, and to it is attached the tube *i*, to convey the blast to any desired point. The water and air which together flow down the pipe *k b*, pass into the bottle. When the water is turned on, the caoutchouc tube *g i* is closed for a moment with the thumb and finger. This starts the water through the siphon, and immediately a continuous and powerful blast of air rushes out through the tube *g i*, and may be carried directly to the blow-pipe. The siphon must be capable of carrying off a larger stream of water than that which is allowed to enter, so that there shall never be more than 3 or 4 c. m. of water in the bottle.

Fig. 19.



The efficiency of the blast depends upon the dimensions of the tubes and the head of water employed; one of the Bunsen pumps in the laboratory of the Institute of Technology used to furnish a blast for the blowpipe is made of half-inch lead pipe and there is a fall of about 30 feet. It is, however, by no means necessary to have so great a fall; a fall of 6 or 8 feet furnishes an efficient blast, but the amount of water used is much larger.

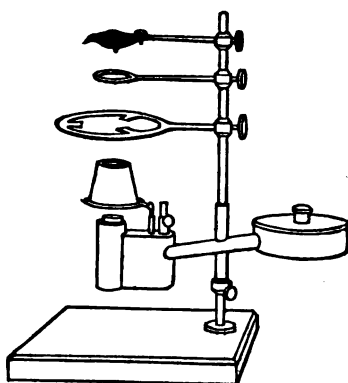
In default of a blast lamp, platinum crucibles may readily be ignited in a fire of coke or anthracite. To this end, place the tightly covered platinum crucible in a somewhat larger crucible of refractory clay or Hessian ware, and pack the space between the two crucibles tightly with calcined magnesia, so that the platinum may nowhere come in contact with the clay. Cover the coarse crucible, and place it, with its contents, in the coal fire, in such a manner that it may be gradually heated; finally, imbed the crucible in the glowing coals and urge the draught of the furnace for half an hour. The degree of heat to which the contents of the platinum crucible may be exposed, in this way, in an efficient fire, is really far greater

than that of the blast lamps above described but the lamps are more convenient than the fire.

The effect of a simple Bunsen's burner may be greatly increased, without the use of any blower, by surrounding its flame with a cylinder of fire clay, 8 inches in diameter by 4 or 5 inches high, and having walls at least 3-8 of an inch thick. The crucible, or other body to be heated, is hung in the middle of this chimney, and is thus exposed not only to the direct heat of the flame, but also to the radiant heat from the clay walls which surround it.

Where no gas is to be had, an alcohol lamp with circular wick, of some one of the numerous forms sold under the name of Berzelius's

Fig. 20.

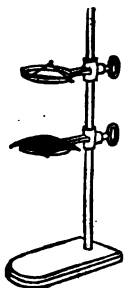


Argand Spirit Lamp (Fig. 20), will be found useful. These argand lamps are usually mounted on a lamp-stand provided with three brass rings; but the fittings of these lamps are all made slender, in order not to carry off too much heat. When it is necessary to heat heavy vessels, other supports must be used.

76. Iron-stand, Tripod, Wire-gauze and Triangle.

— To support vessels over the gas-lamp, an iron stand is used consisting of a stout vertical rod fastened into a heavy, cast-iron foot, and several iron rings of graduated sizes secured to the vertical rod with binding screws; all the rings may be slipped

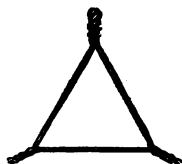
Fig. 21.



off the rod, or any ring may be adjusted at any convenient elevation. The general arrangement is not unlike that of the stand which makes part of the Berzelius lamp (Fig. 20), although simpler and cheaper. As a general rule, it is not best to apply the direct flame to glass and porcelain vessels; hence a piece of iron wire-gauze of medium fineness is stretched loosely over the largest ring, and bent downwards a little for the reception of round-bottomed vessels; on this gauze, flasks and porcelain dishes are usually supported. Crucibles, or dishes, too small for the smallest ring belonging to the stand, are conveniently supported on an equilateral triangle made of three pieces

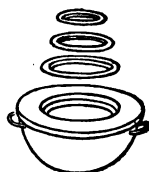
of soft iron wire twisted together at the apices; this triangle is laid on one of the rings of the stand. An iron tripod,—that is, a stout ring supported on three legs,—may often be used instead of the stand above described, but it is not so generally useful because of the difficulty of adjusting it at various heights; with a sufficiency of wooden blocks wherewith to raise the lamp or the tripod as occasion may require, it may be made available.

Fig. 22.



77. Water-bath and Sand-bath.—It is often necessary to evaporate solutions, or to dry precipitates at a moderate temperature which can permanently be kept below a certain known limit; thus, when an aqueous solution is to be quietly evaporated without spiriting or jumping, the temperature of the solution must never be suffered to rise above the boiling-point of water, nor even quite to reach this point. This quiet evaporation is best effected by the use of a water-bath,—a copper cup whose top is made of concentric rings of different diameters to adapt it to dishes of various sizes (Fig. 23).

Fig. 23.



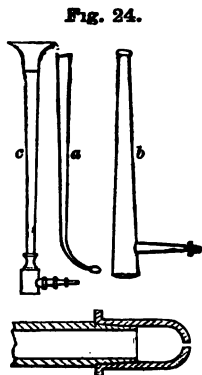
This cup, two thirds full of water, is supported on the iron-stand over the lamp, and the dish containing the solution to be evaporated is placed on that one of the several rings which will permit the greater part of the dish to sink into the copper cup. The steam rising from the water impinges upon the bottom of the dish, and brings the liquid within it to a temperature which insures the evaporation of the water, but will not cause any actual ebullition. The water in the copper cup must never be allowed to boil away. Wherever a constant supply of steam is at hand, as in buildings warmed by steam, the copper cup above described may be converted into a steam-bath by attaching it to a steam-pipe by means of a small tube provided with a stop-cock.

An empty tomato-can furnished with rings as above may take the place of the copper cup, and, in fact, a cheap but serviceable water-bath may be made from a quart milk-can, oil-can, tea-canister, or any similarly shaped tin vessel, by inserting the stem of a glass funnel into the neck of the can through a well-fitting cork. In this funnel the dish containing the liquor to be evaporated rests. The can contains the water, which is to be kept just boiling. On account of the shape

of the funnel, dishes of various sizes can be used with the same apparatus.

When a gradual and equable heat higher than can be obtained upon the water-bath is required, a sand-bath will sometimes be found useful. A cheap and convenient sand-bath may be made by beating a disk of thin sheet iron, about four inches in diameter, into the form of a saucer or shallow pan, and placing within it a small quantity of dry sand. The dish or flask to be heated is imbedded in the sand, and the apparatus placed upon a ring of the iron-stand over a gas-lamp.

73. **Blowpipes.**—The mouth-blowpipe in its simplest form is a tube bent near one extremity at a right angle. Fig. 24, *a*, represents a common form of blowpipe used by jewellers. The blowpipe is rendered more convenient by the addition of a mouth-piece and a chamber near the right angle for the condensation of moisture. Fig. 24, *b* and *c*, represent different forms of blowpipe thus furnished.



The cheapest and best form of mouth blowpipe for chemical purposes is a tube of tin-plate, about 18 c. m. long, 2 c. m. broad at one end, and tapering to 0.7 c. m. at the other (Fig. 24, *b*); the broad end is closed, and serves to retain the moisture; a little above this closed end a small cylindrical tube of brass about 5 c. m. long is soldered in at right angles; this brass tube is slightly conical at the end, and carries a small nozzle or tip, which may be made either of brass or platinum. The tip should be drilled out of a solid piece of metal, and should not be fastened upon the brass tube with a screw. A trumpet-shaped mouth-piece of horn or boxwood is a convenient, though by no means essential, addition to this blowpipe. For convenience in cleaning and packing, blowpipes are often made in several pieces, as is the one represented in Fig. 24, *c*.

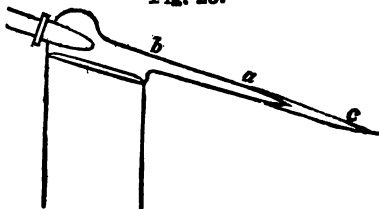
The blowpipe may be used with a candle, with gas or with any hand-lamp proper for burning oil, petroleum or any of the so-called *burning fluids*, provided that the form of the lamp below the wick-holder is such as to permit the close approach of the object to be heated to the side of the wick. When a lamp is used, a wick about 1.2 c. m. long and 0.5 c. m. broad is more convenient than a round or narrow wick. The wick-holder should be filed off on its longer dimension a little obliquely, and the wick cut parallel to the holder,

in order that the blowpipe flame may be directed downwards when necessary (Figs. 25 and 26). A gas flame suitable for the blowpipe is readily obtained by slipping a narrow brass tube (*t*), open at both ends, into the tube *f* of Bunsen's burner. (See Fig. 13.) This blowpipe-tube must be long enough to close the air apertures in the tube *f*, and should be pinched together and filed off obliquely on top; it may usually be obtained with the burner from dealers in chemical ware.

To use the mouth blowpipe, place the open end of the tube between the lips, or, if the pipe is provided with a mouth-piece, press the trumpet-shaped mouth-piece against the lips; fill the mouth with air till the cheeks are widely distended, and insert the tip in the flame of a lamp or candle; close the communication between the lungs and the mouth, and force a current of air through the tube by squeezing the air in the mouth with the muscles of the cheeks, breathing, in the meantime, regularly and quietly through the nostrils. The knack of blowing a steady stream for several minutes at a time, is readily acquired by a little practice. It will be at once observed that the appearance of the flame varies considerably, according to the strength of the blast and the position of the jet with reference to the wick.

When the jet of the blowpipe is inserted into the middle of a candle-flame, or is placed in the lamp-flame in the position shown in Fig. 25, and a strong blast is forced through the tube, a long, blue cone of flame, *ab*, is produced, beyond and outside of which stretches a more or less colored outer cone towards *c*.

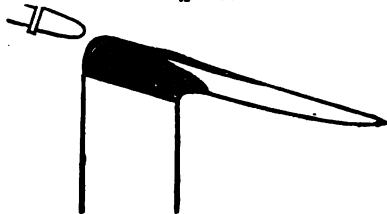
Fig. 25.



The point of greatest heat in this flame is at the point of the inner blue cone, because the combustible gases are there supplied with just the quantity of oxygen necessary to consume them, but between this point and the extremity of the flame the combustion is concentrated and intense. The greater part of the flame thus produced is *oxidizing* in its effect, and this flame is technically called the *oxidizing flame*. From the point *a* of the inner blue cone, the heat of the flame diminishes in both directions, towards *b*, on the one hand, and towards *c* on the other; most substances require the temperature which is found between *a* and *c*. Oxidation takes place most rapidly at, or just beyond the point *c* of the flame, provided that the temperature at this point is high enough for the special substance to be heated.

A flame of precisely the opposite chemical effect may be produced with the blowpipe. To obtain a good *reducing* flame, it is necessary to place the tip of the blowpipe, not within, but just outside of the

Fig. 26.



flame, and to blow rather over than through the middle of the flame (Fig. 26)

In this manner, the flame is less altered in its general character than in the former case, the chief part consisting of a large, luminous cone, containing a quantity of free carbon in a state of intense

ignition, and just in the condition for taking up oxygen. This flame is, therefore, *reducing* in its effect, and is technically called the *reducing* flame. The substance which is to be reduced by exposure

to this flame, should be completely covered up by the luminous cone, so that contact with the air may be entirely avoided. It is to be observed that, whereas to produce an effective oxidizing flame a strong blast of air is desirable, to get a good reducing flame, the operator should blow gently, with only enough force to divert the lamp-flame.

Fig. 27.



Substances to be heated in the blowpipe flame, are supported, sometimes on charcoal, and sometimes on platinum foil or wire, or in platinum spoons or forceps.

Charcoal is especially suitable for a support in experiments of reduction. With reference to the choice of charcoal for blowpipe experiments, see § 81. The manner of holding the blowpipe is illustrated by Fig. 27.

79. Platinum Foil and Wire. — Pincers. — A piece of platinum foil about 1 1-2 inches long, and 1 inch wide will be sufficient. The foil should be at least so thick that it does not crinkle when wiped; and it is more economical to get foil which is too thick than too thin, for it requires frequent cleaning. To keep foil in good order it should be frequently scoured with fine moist sand, and in case the foil becomes wrinkled it may be burnished by placing it upon the bottom of an inverted agate or porcelain mortar and rubbing it strongly with the pestle.

A bit of platinum wire, not stouter than the wire of a small pin and about 8 inches long, will last a long time with careful usage. It may be cleaned by long-continued boiling in water. A small loop about as large as this O, should be bent at each end of the wire.

When platinum foil is to be heated, it may be held at one end with a pair of the small steel pincers known as jewellers' tweezers. A piece of platinum wire, as long as the one above described, can be held in the fingers without inconvenience, for platinum is, comparatively speaking, a bad conductor of heat. Pieces of wire, too short to be held, may be made serviceable by thrusting one end of the wire into the end of a glass rod or closed tube which has been softened in the blowpipe flame.

80. Platinum Crucibles.—For several of the operations of quantitative analysis as now practised, platinum crucibles are indispensable, and though not absolutely necessary for the profitable study of qualitative analysis, one of these vessels will often be found convenient by the student of the elements of analysis. It will be well, therefore, for the student, who proposes to continue his chemical studies beyond qualitative analysis, to procure a platinum crucible once for all. A crucible of the capacity of about 20 cubic centimetres will be large enough for most uses; it should be cylindrical rather than flaring, and should be provided with a loose cover in the form of a shallow dish. For the purposes of this book, however, a small crucible holding 7 or 8 cubic centimetres answers every purpose and a cover is not essential.

No other metal, and no mixture of substances from which a metal can be reduced, must ever be heated in a platinum crucible, or upon platinum foil or wire, for platinum forms alloys with other metals, and these alloys are much more fusible than platinum itself. If once alloyed with a baser metal, the platinum ceases to be applicable to its peculiar uses.

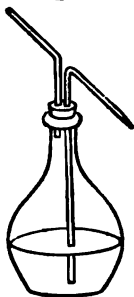
Platinum may be cleaned by boiling it in either nitric or chlorhydric acid, by fusing acid sulphate of sodium upon it, or by scouring it with fine sand. Aqua regia and chlorine-water dissolve platinum; the sulphides, cyanides, and hydrates of sodium and potassium, when fused in platinum vessels, slowly attack the metal.

81. Wash-bottle.—A wash-bottle is a flask with a uniformly thin bottom closed with a sound cork or caoutchouc stopper through which pass two glass tubes, as shown in Fig. 29.

Fig. 28.



Fig. 29.

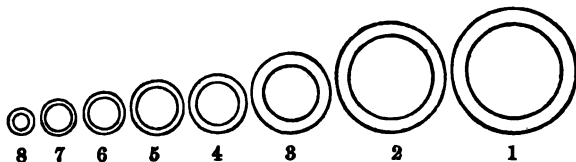


The outer end of the longer tube is drawn to a moderately fine point. A short bend near the bottom of this longer tube in the same plane and direction as the upper bend is of some use, because it enables the operator to empty the flask more completely by inclining it. By blowing into the short tube, a stream of water will be driven out of the long tube with considerable force. This force with which the stream is projected adapts the apparatus to removing precipitates from the sides of vessels as well as to washing them on filters. For use in analytical operations, it is often convenient to attach a caoutchouc tube 12 or 15 c. m. long to the tube through which the air is blown; this flexible tube should be provided with a glass mouth-piece, consisting of a bit of glass tubing about 3 c. m. long. As the wash-bottle is often filled with hot or even boiling water, it may be improved by binding about its neck a ring of cork, or winding the neck closely with smooth cord. It may then be handled without inconvenience, when hot.

The method of making a wash-bottle is described in the following paragraphs.

82. Glass Tubing. — Two qualities of glass tubing are used in chemical experiments, that which softens readily in the flame of a gas- or spirit-lamp, and that which fuses with extreme difficulty in the flame of the blast-lamp. These two qualities are distinguished by the terms *soft* and *hard* glass. Soft glass is to be preferred for all uses except the intense heating, or ignition, of dry substances. Fig. 30 represents the common sizes of glass tubing, both hard and

Fig. 30.

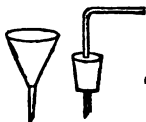


soft, and shows also the proper thickness of the glass walls for each size. The numbers ranging from 4 to 8 are best suited for use in qualitative analysis.

83. Stirring-rods. — Cut a short stick of glass rod, No. 8 or 7, into pieces four or five inches long (see the next paragraph), and round the sharp ends by fusion in the blowpipe flame.

84. Cutting and Cracking Glass.—Glass tubing and glass rod must generally be cut to the length required for any particular apparatus. A sharp triangular file is used for this purpose. The stick of tubing, or rod, to be cut is laid upon a table, and a deep scratch is made with the file at the place where the fracture is to be made. The stick is then grasped with the two hands, one on each side of the mark, while the thumbs are brought together just at the scratch. By pushing with the thumbs and pulling in the opposite direction with the fingers, the stick is broken squarely at the scratch, just as a stick of candy or dry twig may be broken. The sharp edges of the fracture should invariably be made smooth, either with a wet file, or by softening the end of the tube or rod in the lamp. (App., § 85.) Tubes or rods of sizes four to eight inclusive may readily be cut in this manner; the larger sizes are divided with more difficulty, and it is often necessary to make the file-mark both long and deep. An even fracture is not always to be obtained with large tubes. The lower ends of glass funnels, and those ends of gas delivery-tubes which enter the bottle or flask in which the gas is generated, should be filed off, or ground off on a grindstone, obliquely (Fig. 31), to facilitate the dropping of liquids from such extremities.

Fig. 31.



In order to cut glass plates, the glazier's diamond must be resorted to. For the cutting of exceedingly thin glass tubes and of other glass ware, like flasks, retorts and bottles, still other means are resorted to, based upon the sudden and unequal application of heat. The process divides itself into two parts, the producing of a crack in the required place, and the subsequent guiding of this crack in the desired direction. To produce a crack, a scratch must be made with the file, and to this scratch a pointed bit of red-hot charcoal, or the jet of flame produced by the mouth blowpipe, or a very fine gas-flame, or a red-hot glass-rod may be applied. If the heat does not produce a crack, a wet stick or file may be touched upon the hot spot. Upon any part of a glass surface except the edge, it is not possible to control perfectly the direction and extent of this first crack; at an edge a small crack may be started with tolerable certainty by carrying the file-mark entirely *over* the edge. To guide the crack thus started, a pointed bit of charcoal or slow-match may be used. The hot point must be kept on the glass from 1 c. m. to 0.5 c. m. in advance of the point of the crack. The crack will follow the hot point, and may therefore be carried in any desired direction. By turning and blowing upon the coal or slow-match, the

point may be kept sufficiently hot. Whenever the place of experiment is supplied with common illuminating gas, a very small jet of burning gas may be advantageously substituted for the hot coal or slow match. To obtain such a sharp jet, a piece of hard glass tube, No. 4, 10 c. m. long, and drawn to a very fine point (App., § 85), should be placed in the caoutchouc tube which ordinarily delivers the gas to the gas-lamp, and the gas should be lighted at the fine extremity. The burning jet should have a fine point, and should not exceed 1.5 c. m. in length. By a judicious use of these simple tools, broken tubes, beakers, flasks, retorts and bottles may often be made to yield very useful articles of apparatus. No sharp edges should be allowed to remain upon glass apparatus. The durability of the apparatus itself, and of the corks and caoutchouc stoppers and tubing used with it, will be much greater, if all sharp edges are removed with the file, or, still better, rounded in the lamp.

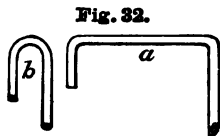
85. Bending and Closing Glass Tubes. — Tubing of sizes four to eight inclusive can generally be worked in the common gas- or spirit lamp; for larger tubes the blast-lamp is necessary. (App., § 75.) Glass tubing must not be introduced suddenly into the hottest part of the flame, lest it crack. Neither should a hot tube be taken from the flame and laid at once upon a cold surface. Gradual heating and gradual cooling are alike necessary, and are the more essential the thicker the glass; very thin glass will sometimes bear the most sudden changes of temperature, but thick glass and glass of uneven thickness absolutely require slow heating and annealing. When the end of a tube is to be heated, as in rounding sharp edges, more care is required in consequence of the great facility with which cracks start at an edge. A tube should, therefore, always be brought first into the current of hot air beyond the actual flame of the gas- or spirit-lamp, and there thoroughly warmed, before it is introduced into the flame itself. If a blast-lamp is employed, the tube may be warmed in the smoky flame, before the blast is turned on, and may subsequently be annealed in the same manner; the deposited soot will be burnt off in the first instance, and in the last may be wiped off when the tube is cold. In heating a tube, whether for bending, drawing, or closing, the tube must be *constantly* turned between the fingers, and also moved a little to the right and left, in order that it may be uniformly heated all round, and that the temperature of the neighboring parts may be duly raised. If a tube, or rod, is to be heated at any part but an end, it should be held between the thumb and first two fingers of each hand in such a manner that the hands shall be below the tube or rod, with the palms upward,

while the lamp-flame is between the hands. When the end of a tube or rod is to be heated, it is best to begin by warming the tube or rod about 2 c. m. from the end, and thence to proceed slowly to the end.

The best glass will not be blackened or discolored during heating. Blackening occurs in glass which, like ordinary flint glass, contains lead as an ingredient. Glass containing much lead is not well adapted for chemical uses. The blackening may sometimes be removed by putting the glass in the upper or outer part of the flame, where the reducing gases are consumed, and the air has the best access to the glass. The blackening may be altogether avoided by always keeping the glass in the oxidizing part of the flame.

Glass begins to soften and bend below a visible red heat. The condition of the glass is judged of as much by the fingers as the eye; the hands feel the yielding of the glass, either to bending, pushing, or pulling, better than the eye can see the change of color or form. It may be bent as soon as it yields in the hands, but can be drawn out only when much hotter than this. Glass tubing, however, should not be bent at too low a temperature; the curves made at too low a heat are apt to be flattened, of unequal thickness on the convex and concave sides, and brittle.

In bending tubing to make gas-delivery tubes and the like, attention should be paid to the following points: 1st, the glass should be equally hot on all sides; 2d, it should not be twisted, pulled out, or pushed together during the heating; 3d, the bore of the tube at the bend should be kept round, and not altered in size; 4th, if two or more bends be made in the same piece of tubing (Fig. 32, *a*), they should all be in the same plane, so that the finished tube will lie flat upon the level table.



When a tube or rod is to be bent or drawn close to its extremity, a temporary handle may be attached to it by softening the end of the tube or rod, and pressing against the soft glass a fragment of glass tube, which will adhere strongly to the softened end. The handle may subsequently be removed by a slight blow, or by the aid of a file. If a considerable bend is to be made, so that the angle between the arms will be very small or nothing, as in a siphon, for example, the curvature cannot be well produced at one place in the tube, but should be made by heating, progressively, several centimetres of the tube, and bending continuously from one end of the heated portion to the other (Fig. 32, *b*). Small and thick tube may be bent more sharply than large or thin tube.

A lamp for bending glass tubing better than the ordinary form of the Bunsen burner, is one the tube of which is flattened out so as to give a thin but broad flame of the same character as the ordinary

Fig. 33.



lamp but in shape more like a bat-wing burner. (See Fig. 33.) The tube is placed in this flame and turned round and round until it reaches the proper temperature; it is then withdrawn from the flame and bent. In this way a regular curve may be obtained and the sides of the tube do not collapse.

In order to draw a glass tube down to a finer bore, it is simply necessary to thoroughly soften on all sides one or two centimetres' length of the tube and then taking the glass from the flame, pull the parts asunder by a cautious movement of the hands.

The larger the heated portion of glass, the longer will be the tube thus formed. Its length and fineness also increase with the rapidity of motion of the hands. If it is desirable that the finer tube should have thicker walls in proportion to its bore than the original tube, it is only necessary to keep the heated portion soft for two or three minutes before drawing out the tube, pressing the parts slightly together the while. By this process the glass will be thickened at the hot ring.

To obtain a tube closed at one end, it is best to take a piece of

Fig. 34.



tubing, open at both ends, and long enough to make two closed tubes. In the middle of the tube a ring of glass, as narrow as possible, must be made thoroughly soft. The hands are then separated a little, to cause a contraction in diameter at the hot and soft part. The point of the flame must now

be directed, not upon the narrowest part of the tube, but upon what is to be the bottom of the closed tube. This point is indicated by the line *a* in Fig 34. By withdrawing the right hand, the narrow part of the tube is attenuated, and finally melted off, leaving both halves of the original tube closed at one end, but not of the same form; the right-hand half is drawn out into a long point, the other is more roundly closed. It is not possible to close handsomely the two pieces at once. The tube is seldom perfectly finished by the operations; a superfluous knob of glass generally remains upon the end. If small it may be got rid of by heating the whole end of the tube, and blowing moderately with the mouth into

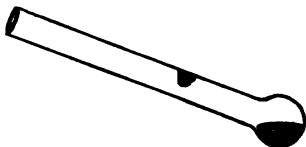
the open end. The knob, being hotter, and therefore softer than any other part, yields to the pressure from within, spreads out and disappears. If the knob is large, it may be drawn off by sticking to it a fragment of tube, and then softening the glass above the junction. The same process may be applied to the too pointed end of the right-hand half of the original tube, or to any misshapen result of an unsuccessful attempt to close a tube, or to any bit of tube which is too short to make two closed tubes. When the closed end of a tube is too thin, it may be strengthened by keeping the whole end at a red heat for two or three minutes, turning the tube constantly between the fingers. It may be said in general of all the preceding operations before the lamp, that success depends on keeping the tube to be heated in constant rotation, in order to secure a uniform temperature on all sides of the tube.

86. Blowing Bulbs. — Bulb-tubes, like the one represented in Fig. 35, are employed for reducing substances capable of forming sublimates upon the cold walls of the tube. They are readily made from bits of tubing, in the flame of Bunsen's burner, or in the common blowpipe flame.

If the bulb desired is large in proportion to the size of the tube on which it is to be made, the walls of the tube must be thickened by rotation in the flame before the bulb can be blown. The thickened portion of glass is then to be heated to a cherry-red, suddenly withdrawn from the flame, and expanded while hot by steadily blowing, or rather pressing air, into the tube with the mouth; the tube must be constantly turned on its axis, not only while in the flame, but also while the bulb is being blown. If too strong or too sudden a pressure be exerted with the mouth, the bulb will be extremely thin and quite useless. By watching the expanding glass, the proper moment for arresting the pressure may usually be determined. If the bulb obtained be not large enough, it may be reheated and enlarged by blowing into it again, provided that a sufficient thickness of glass remain. If a bulb is to be blown in the middle of a piece of tubing, the thickening is effected by gently pressing the ends of the tube together while the glass is red-hot in the place where the bulb is to be.

It is sometimes necessary to make a hole in the side of a tube or

Fig. 35.



other thin glass apparatus. This may be done by directing a pointed flame from the blast-lamp upon the place where the hole is to be, until a small spot is red-hot, and then blowing forcibly into one end of the tube while the other end is closed by the finger; at the hot spot the glass is blown out into a thin bubble, which bursts or may be easily broken off, leaving an aperture in the side of the tube.

It is hoped that these few directions will enable the attentive student to perform, sufficiently well, all the manipulations with glass tubes which the experiments described in this manual require. Much practice will alone give a perfect mastery of the details of glass-blowing.

87. Caoutchouc. — Vulcanized caoutchouc is a most useful substance in the laboratory, on account of its elasticity and because it resists so well most of the corrosive substances with which the chemist deals. It is used in three forms: (1) in tubing of various diameters comparable with the sizes of glass tubing; (2) in stoppers of various sizes to replace corks; (3) in sheets. Caoutchouc tubing may be used to conduct all gases and liquids which do not corrode its substance, provided that the pressure under which the gas or liquid flows be not greater, or their temperature higher, than the texture of the tubing can endure. The flexibility of the tubing is a very obvious advantage in a great variety of cases. Short pieces of such tubing, a few centimetres in length, are much used, under the name of connectors, to make flexible joints in apparatus, of which glass tubing forms part; flexible joints add greatly to the durability of such apparatus, because long glass tubes bent at several angles and connected with heavy objects, like globes, bottles or flasks full of liquid, are almost certain to break even with the most careful usage; gas delivery-tubes, and all considerable lengths of glass tubing should invariably be divided at one or more places, and the pieces joined again with caoutchouc connectors. The ends of glass tubing to be thus connected should be squarely cut, and then rounded in the lamp, in order that no sharp edges may cut the caoutchouc; the internal diameter of the caoutchouc tube must be a little smaller than the external diameter of the glass tubes; the slipping on of the connector is facilitated by wetting the glass. In some cases of delicate quantitative manipulations, in which the tightest possible joints must be secured, the caoutchouc connector is bound on to the glass tube with a silk or smooth linen string; the string is passed as tightly as possible twice round the connector and tied with a square knot; the string should be

moistened in order to prevent it from slipping while the knot is tying.

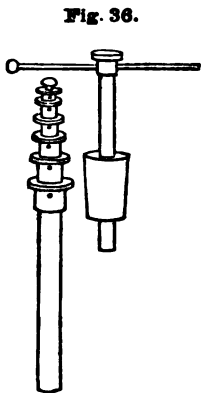
Caoutchouc stoppers of good quality are much more durable than corks, and are in every respect to be preferred. The German stoppers are of excellent shape and quality; the American, being chiefly intended for wine bottles, are apt to be too conical. Caoutchouc stoppers can be bored, like corks (see the next section), by means of suitable cutters, and glass tubes can be fitted into the holes thus made with a tightness unattainable with corks. German stoppers may be bought already provided with one, two, and three holes. It is not well to lay in a large stock of caoutchouc stoppers, for though they last a long time when in constant use, they not infrequently deteriorate when kept in store, becoming hard and somewhat brittle with age.

Pieces of thin sheet caoutchouc are very conveniently used for making tight joints between large tubes of two different sizes, or between the neck of a flask, or bottle, and a large tube which enters it, or between the neck of a retort and the receiver into which it enters. A sufficiently broad and long piece of sheet caoutchouc is considerably stretched, wrapped tightly over the glass parts adjoining the aperture to be closed, and secured in place by a string wound closely about it and tied with a square knot.

88. Corks.—It is often very difficult to obtain sound, elastic corks of fine grain and of size suitable for large flasks and wide-mouthed bottles. On this account, bottles with mouths not too large to be closed with a cork cut across the grain, should be chosen for chemical uses, in preference to bottles which require large corks or bungs cut with the grain, and therefore offering continuous channels for the passage of gases, or even liquids. The kinds sold as champagne corks and as satin corks for phials are suitable for chemical use. The best corks generally need to be softened before using; this softening may be effected by rolling the cork under a board upon the table, or under the foot upon the clean floor, or by gently squeezing it on all sides with the well-known tool expressly adapted for this purpose, and thence called a cork-squeezer. Steaming also softens the hardest corks.

Cork must often be cut with cleanness and precision; a sharp, thin knife, such as shoemakers use, is desirable for this purpose. When a cork has been pared down to reduce its diameter, a flat file may be employed in finishing; the file must be fine enough to leave a smooth surface upon the cork; in filing a cork, a cylindrical, not a conical, form should be aimed at.

In boring holes through corks to receive glass tubes, a hollow cylinder of sheet brass sharpened at one end is a very convenient tool. Fig. 36 represents a set of such little cylinders of graduated sizes, slipping one within the other into a very compact form; a stout wire of the same length as the cylinders, accompanies the set, and serves a double purpose, — passed transversely through two holes in the cap which terminates each cylinder, it gives the hand a better grasp of the tool while penetrating the cork; and when the hole is made, the wire thrust through an opening in the top of the cap expels the little cylinder of cork which else would remain in the cutting cylinder of brass. That cutter, whose diameter is next below that of the glass tube to be inserted in the cork, is always to be selected, and if

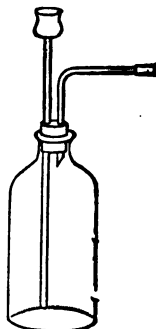


the hole it makes is too small, a round file must be used to enlarge the aperture; the round file, also, often comes in play to smooth the rough sides of a hole made by a dull cork-borer. A pair of small calipers is a very convenient, though by no means essential, tool in determining which size of cutter to employ. A flask which presents sharp or rough edges at the mouth can seldom be tightly corked, for the cork cannot be introduced into the neck without being cut or roughened; such sharp edges must be rounded in the lamp. In thrusting glass tubes through bored corks, the following directions are to be observed: (1.) The end of the tube must not present a sharp edge capable of cutting the cork. (2.) The tube should be grasped very close to the cork, in order to escape cutting the hand which holds the cork, should the tube break; by observing this precaution, the chief cause of breakage, viz., irregular lateral pressure, will be at the same time avoided. (3.) A funnel-tube must never be held by the funnel in driving it through a cork, nor a bent tube grasped at the bend, unless the bend comes immediately above the cork. (4.) If the tube goes very hard through the cork, the application of a little soap and water will facilitate its passage, but if soap is used, the tube can seldom be withdrawn from the cork after the latter has become dry. (5.) The tube must not be pushed straight into the cork, but screwed in, as it were, with a slow rotary as well as onward motion. Joints made with corks should always be tested before the apparatus is used, by blowing into the apparatus, and at the same time stopping up all legitimate outlets.

Any leakage is revealed by the disappearance of the pressure created. To the same end, air may be sucked out of an apparatus and its tightness proved by the permanence of the partial vacuum. To attempt to use a leaky cork is generally to waste time and labor, and to insure the failure of the experiment.

89. Gas-bottle. — Figure 37 represents a gas-bottle fitted for evolving sulphuretted hydrogen, carbonic acid, and other gases which can be prepared without heat. A straight glass tube of convenient length is slipped into the caoutchouc connector at the right to carry the gas into the solution to be tested. The neck of the bottle should be rather narrow, since it is difficult to obtain tight stoppers for bottles with wide mouths, but must nevertheless be wide enough to admit a cork, or better a caoutchouc stopper, capable of carrying both the delivery and the thistle tubes.

Fig. 37.



To prepare, for example, sulphuretted hydrogen gas, put a tablespoonful of fragments of sulphide of iron in the bottom of the bottle, replace the cork with its tubes, and press, or rather twist, it tightly into the neck of the bottle; pour in enough water through the thistle-tube to seal the lower end of that tube, and finally as much concentrated sulphuric acid as would be equal to a tenth or a twelfth of the volume of the water.

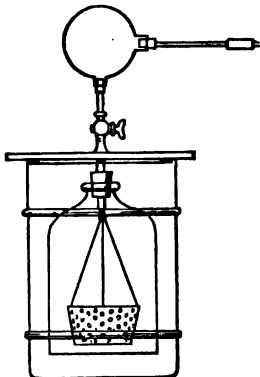
At the start it is well thus to mix strong acid with the water in the bottle, for the heat generated by the union of the two liquids serves to warm the apparatus, and to facilitate the decomposition of the sulphide of iron; but it must be remembered that strong sulphuric acid is by itself unfit for generating sulphuretted hydrogen, and that the evolution of gas would be checked if much of it were added. When the flow of gas ceases, pour a small portion of dilute sulphuric acid into the thistle-tube, and repeat this operation as often as may be necessary to maintain a constant stream of gas. Dilute acid fit for this purpose may be prepared by mixing 1 volume of strong sulphuric acid with 14 volumes of water; — the water should be well stirred and the acid poured into it in a fine stream.

In precipitating the members of Classes II and III with sulphuretted hydrogen, the gas delivery-tube should not dip deeper than about an inch beneath the surface of the liquid in the beaker. A rapid current of gas is useless and wasteful. The best method of operating is to pour dilute sulphuric acid into the thistle-tube in

such quantity that the bubbles of gas may follow one another slowly enough to be counted without effort.

90. Self-regulating Gas-generator. — An apparatus which is always ready to deliver a constant stream of sulphuretted hydrogen, and yet does not generate the gas except when it is immediately wanted for use, is a great convenience in an active laboratory.

Fig. 38.



The same remark applies to the two gases, hydrogen and carbonic acid, which are likewise used in considerable quantities in quantitative analysis, and which can be conveniently generated in precisely the same form of apparatus which is advantageous for sulphuretted hydrogen. Such a generator may be made of divers dimensions. The following directions, with the accompanying figure (Fig. 38), will enable the student to construct an apparatus of convenient size. Procure a glass cylinder 20 or 25 c. m. in diameter and 30 or 35 c. m. high; ribbed candy jars are sometimes to be had of about this size; procure also a stout tubulated bell-glass

10 or 12 c. m. wide and 5 or 7 c. m. shorter than the cylinder. Get a basket of sheet-lead 7.5 c. m. deep and 2.5 c. m. narrower than the bell-glass, and bore a number of small holes in the sides and bottom of this basket. Cast a circular plate of lead 7 m. m. thick and of a diameter 4 c. m. larger than that of the glass cylinder; on what is intended for its under side solder three equidistant leaden strips, or a continuous ring of lead, to keep the plate in proper position as a cover for the cylinder. Fit tightly to each end of a good brass gas-cock a piece of brass tube 8 c. m. long, 1.5 to 2 c. m. wide, and stout in metal. Perforate the centre of the leaden plate, so that one of these tubes will snugly pass through the orifice, and secure it by solder, leaving 5 c. m. of the tube projecting below the plate. Attach to the lower end of this tube a stout hook on which to hang the leaden basket. By means of a sound cork and common sealing-wax, or a cement made of oil mixed with red and white lead, fasten this tube into the tubulure of the bell-glass air-tight, and so firmly that the joint will bear a weight of several pounds. Hang the basket by means of copper wire within the bell 5 c. m. above the bottom of the latter. To the tube which extends above the stop-

cock attach by a good cork the neck of a tubulated receiver of 100 or 150 c. c. capacity, the interior of which has been loosely stuffed with cotton. Into the second tubulure of the receiver fit tightly the delivery-tube carrying a caoutchouc connector; into this connector can be fitted a tube adapted to convey the gas in any desired direction. When many persons use the same generator, each person must bring his own tube.

To charge the apparatus, fill the cylinder with dilute acid to within 10 or 12 c. m. of the top, fill the basket with fragments of sulphide of iron, hang the basket in the bell, and put the bell-glass full of air into its place with the stop-cock closed. On opening the cock, the weight of the acid expels the air from the bell, the acid comes in contact with the solid in the basket, and a steady supply of gas is generated until either the acid is saturated or the solid dissolved; if the cock be closed, the gas accumulates in the bell, and pushes the acid below the basket so that all action ceases. In cold weather the apparatus must be kept in a warm place. For generating sulphuretted hydrogen, sulphuric acid diluted with fourteen parts of water is used; for hydrogen, zinc and sulphuric acid diluted with four or five parts of water; while for carbonic acid, chalk and muriatic acid diluted with two or three parts of water, should be taken.

§1. Mortars.—Whenever the substance to be analyzed occurs in the form of large pieces or coarse powder, it should, as a general rule, be pulverized by mechanical means before subjecting it to the action of solvents. Mortars of iron, steel, agate or porcelain are used for this purpose, according to the character of the substance to be powdered.

An iron mortar is useful for coarse work and for effecting the first rough breaking up of substances which are subsequently powdered in the agate or porcelain mortar. If there be any risk of fragments being thrown out of the mortar, it should be covered with a cloth or piece of stiff paper, having a hole in the middle through which the pestle may be passed. Instead of the common iron mortar, a small steel mortar, of the kind called diamond mortars by dealers in chemical ware, may be used for crushing minerals. Pieces of stone, minerals, and lumps of brittle metals may be safely broken into fragments suitable for the mortar by wrapping them in strong paper, laying them so enclosed upon an anvil and striking them with a heavy hammer. The paper envelope retains the broken particles which might otherwise fly about in a dangerous manner, and be lost.

The best porcelain mortars are those known by the name of

Wedgewood-ware, but there are many cheaper substitutes. Porcelain mortars will not bear sharp and heavy blows; they are intended rather for grinding or triturating saline substances than for hammering; the pestle may either be formed of one piece of porcelain, or a piece of porcelain cemented to a wooden handle; the latter is the less desirable form of pestle. Unglazed porcelain mortars are to be preferred. In selecting mortars, the following points should be attended to, — 1st, the mortar should not be porous; it ought not to absorb strong acids or any colored fluid, even if such liquids be allowed to stand for hours in the mortar; 2d, it should be very hard, and its pestle should be of the same hardness; 3d, it should be sound; 4th, it should have a lip for the convenience of pouring out liquids and fine powders. As a rule, porcelain mortars will not endure sudden changes of temperature. They may be cleaned by rubbing in them a little sand soaked in nitric or sulphuric acid, or if acids are not appropriate, in caustic soda.

Agate mortars are only intended for trituration; a blow would break them. They are exceedingly hard, and impermeable. The material is so precious and so hard to work, that agate mortars are always small. The pestles are generally inconveniently short, — a difficulty which may be remedied by fitting the agate pestle into a wooden handle.

In all grinding operations in mortars, whether of porcelain or agate, it is expedient to put only a small quantity of the substance to be powdered into the mortar at once. The operation of powdering will be facilitated by sifting the matter as fast as it is powdered, returning to the mortar the particles which are too large to pass through the sieve.

92. Spatulæ. — For transferring substances in powder, or in small grains or crystals, from one vessel to another, spatulæ and scoops made of horn or bone are convenient tools. A coarse bone paper-knife makes a good spatula for laboratory use. Cards, free from glaze and enamel, are excellent substitutes for spatulæ.

NOTE. — In the place of the "Bunsen pump" mentioned in §§ 72 and 75, may be used, where there is sufficient head of water, "a jet-aspirator" described by Professor Richards in the "The American Journal of Science," VIII (1874), p. 412. The laboratories of the Institute of Technology and some other laboratories are now furnished with such apparatus (made of brass, by Thomas F. McGann, 104 Portland St., Boston), both for ordinary filtration and for driving the blast-lamps.

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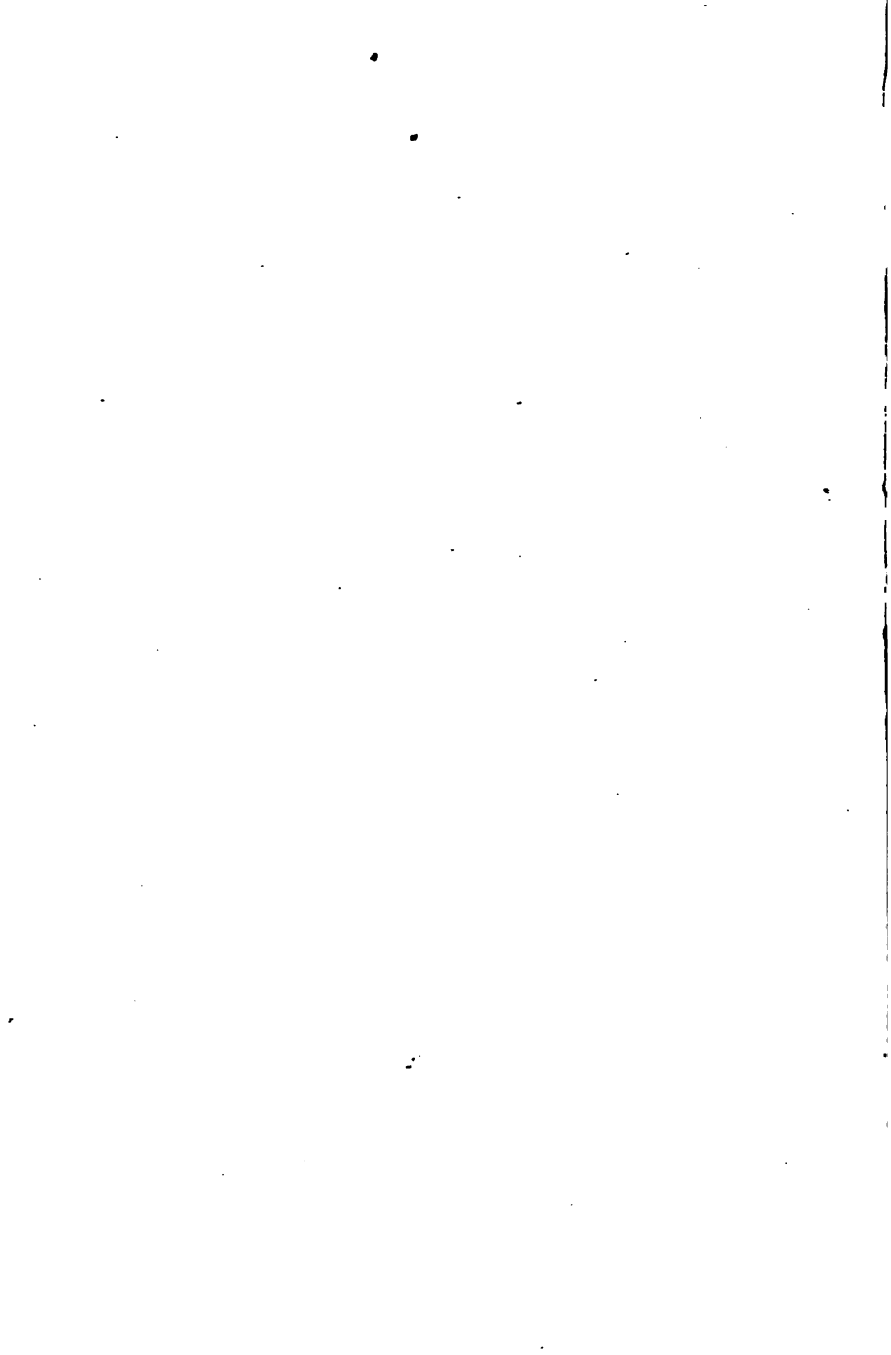
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